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MATHEMATICS

SIMPLEST TRIGONOMETRICAL SUMS WITH PRIMES

By I. VINOGRADOW, Member of the Academy

In the present note we give estimations of the simplest trigonometrical sums with primes. These estimations are near to the best possible ones and we obtain them by application of our general method (1) and partly by use of the well-known method due to Viggo Brun. A certain inconsiderable part of my results (for small q) may be also obtained as a direct conclusion from the theorems concerning the distribution of primes in an arithmetical progression and known before the issue of my paper of 1937 (Titchmarsh, Page, Siegel, Estermann).

We use this opportunity to communicate our new estimations of the usual trigonometrical sums. As before we use the notation $A \ll B$ in the sense of $A = O(B)$.

1. Let n be a positive constant integer, $N > 2$, $r = \log N$, q — an integer, $(a, q) = 1$,

$$S = \sum_{N-A<p\leqslant N} e^{2\pi i \frac{a}{q} p^n},$$

where p runs over primes. Then we have the following theorems.

Theorem 1. *Let ε be a positive constant $\leqslant \frac{1}{3}$, η — an arbitrary small positive constant $< \varepsilon$.*

$$Ne^{-r1-2\varepsilon} \ll A \leqslant N,\ 0 < q \leqslant e^{r^\varepsilon}.$$

Then we have

$$S \ll Ar^{3\varepsilon-1} q^{\eta-\frac{1}{2}}.$$

Theorem 2. *Let ε, η and h be arbitrary small positive constants < 1, σ and α constants satisfying the condition*

$$4\alpha + 6\sigma = \frac{1}{1+h}.$$

Further take

$$N^{1-\alpha} \leqslant A \leqslant N,\ e^{r^\varepsilon} < q \leqslant N^\sigma.$$

Then we have

$$S \ll Aq^{\eta-\frac{1}{2}}.$$

Theorem 3. *Let η and h be arbitrary small positive constants < 1, ε, σ and α constants satisfying the conditions*

$$0 < \varepsilon < \sigma, \quad 3\alpha + 5\sigma = \frac{1}{1+h}.$$

Further let

$$N^{1-\alpha} \leqslant A \leqslant N, \quad N^{\varepsilon} < q \leqslant N^{\sigma}.$$

Then we have

$$S \ll A q^{\eta - \frac{1}{2}}.$$

Remark. However, in the case $n=1$ is more useful to apply the method used in one of my previous papers (2). Then theorems 2 and 3 are true for more wide conditions.

2. In one of my recent papers (3) we gave general theorems concerning the estimation of trigonometrical sums with numerical values of the coefficients of the estimations. However, by a slight modification of the computations we can significantly improve these coefficients. A complete account of the mentioned theorems in this improved form will be given in our monograph which will appear not very soon. But as these theorems have important applications, we state here the improved formulations of them.

Theorem 4. *Let n be an integer $\geqslant 13$, $\nu_1 = \frac{1}{n+1}$, m — an integer > 0, Q — an integer, P — an integer > 0, $a_{n+1}, \ldots, a_1$ — real numbers,*

$$a_{n+1} = \frac{a}{q} + \frac{\theta}{q^2}, \quad (a, q) = 1, \quad |\theta| \leqslant 1,$$

$$f(x) = a_{n+1} x^{n+1} + \ldots + a_1 x, \quad S = \sum_{x=Q+1}^{Q+P} e^{2\pi i m f(x)}.$$

Then we have

1. $|S| < 15nPq^{-\rho}$, $\rho = \frac{1}{(n+1)^3 \log (n+1)}$,

if

$$1 \leqslant q \leqslant P, \quad m \leqslant q^{\nu_1^3}.$$

2. $|S| < 7.5nP^{1-\rho}$, $\rho = \frac{1}{(n+1)^3 \log^{\mu} (n+1)}$,

if

$$P \leqslant q \leqslant P^{n}, \quad q = P^{\mu}, \quad m \leqslant P^{\nu_1^3}.$$

3. $|S| < 7.5 \frac{n}{\tau} P^{1-\rho}$, $\rho = \frac{\tau}{(n+1)^3 \log \frac{n(n+1)}{\tau}}$,

if

$$P \leqslant q < P^{n+1}, \quad q = P^{n+1-\tau}, \quad m \leqslant P^{\tau \nu_1^3}.$$

Addition to Theorem 4. With the notation of theorem 4 we have for any positive value of m correspondingly to the three cases of theorem 4:

1. $|S| < 15\, n m^{\frac{3}{2}\rho} P q^{-\rho}$
2. $|S| < 7.5\, n m^{\frac{3}{2}\rho} P^{1-\rho}$
3. $|S| < 7.5 \frac{n}{\tau} m^{\frac{3}{2}\rho} P^{1-\rho}$.

Theorem 5. *Let n be an integer $\geqslant 14$, Q and P — integers, $P > 0$, $F(z)$ — a real function in the interval*

$$Q < z \leqslant Q + P$$

satisfying the conditions

$$\frac{1}{A} \leqslant \frac{F^{(n)}(z)}{n!} \leqslant \frac{l}{A}, \quad \left| \frac{F^{(n+1)}(z)}{(n+1)!} \right| \leqslant \frac{f}{AP^{\frac{2}{3}}};$$

where

$$P \leqslant A \leqslant P^2; \; l \leqslant 2^n, \; f \leqslant 2^n.$$

Further let

$$S = \sum_{z=Q+1}^{Q+P} e^{2\pi i F(z)}.$$

Then we have

$$|S| < 7.5nP^{1-\rho}, \; \rho = \frac{1}{(n+1)^3 \log 2(n+1)}.$$

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PHYSICS

ULTRA-VIOLET ABSORPTION SPECTRUM AND FLUORESCENCE OF BENZIDINE VAPOURS

By A. T. VARTANIAN

(Communicated by A. N. Terenin, Member of the Academy, 11. III. 1939)

The ultra-violet absorption spectrum of the vapours of organic compounds possessing two benzene nuclei has been investigated by Pervis(1) and Castille(2). It was ascertained that the absorption spectrum of diphenyl ($C_6H_5 \cdot C_6H_5$) located in the region of $\lambda = 2200—2700$ Å and that of diphenylamine ($C_6H_5NH \cdot C_6H_5$) located in the region of $\lambda = 2400—3000$ Å (3) are continuous throughout, whereas the absorption spectra of the vapours of diphenylmethane ($C_6H_5CH_2 \cdot C_6H_5$) and of dibenzyl ($C_6H_5 \cdot CH_2 \cdot CH_2 \cdot C_6H_5$) have a clearly pronounced structure in the region of $\lambda = 2700—2400$ Å, which appears similar to the ultra-violet absorption spectrum of benzyl vapours(4) and is caused by an electronic transition in the phenyl group. At the same time the disturbing effect of identical groups of atoms is so considerable as to deprive the absorption spectrum of diphenyl of any structure. The availability of the $-\overset{H}{\underset{H}{C}}-$ group in diphenyl-methane and dibenzyl lowers in a great measure the interaction of phenyl radicals, which fact is responsible for the appearance of structure. The same phenomenon is observable also in the case of the solutions of these compounds (5). Thus, in the case of diphenyl-methane and dibenzyl each radical retains its own, though strongly disturbed, electronic system.*

In the case of simplest derivatives of benzene the influence of a substitute (non-identical groups of atoms: $-CH_3$, $-C_2H_5$, $-OH$, $-Cl$, $-NH_2$, and so on) tells upon the position of the absorption region, as well as upon the magnitude of the oscillatory quanta. All these derivatives have absorption spectra which, though being very complex, are yet highly discrete. Moreover, in the case of amino-derivatives it is firmly established that two regions of absorption are related to independent electronic transitions in two chromophore groups. For instance, in an aniline molecule such chromophores are: $-C_6H_5$ and $-NH_2$(6,7). It follows from the aforesaid that the influence of the amino-group upon the phenyl group and vice versa can be characterized as disturbing, wherefore a common electronic system fails to exist for these molecules.

* It should be noted that in the case when an electronic system common to the whole chain of atoms is available (the existence of a conjugated bond), the rupture of the chain and the introduction of an $-\overset{H}{\underset{H}{C}}-$ group brings about an effect contrary to the above stated, viz. the spectrum becomes diffuse and is displaced in the direction of short wave lengths.

It appeared of interest to elucidate the following question: in what measure these relations hold true in the case of the amino-derivatives of diphenyl. As investigation material, benzidine was selected (p—p'-diaminodiphenyl, $H_2N.C_6H_4.C_6H_4.NH_2$) which may be considered as the progenitor for a number of azo-dyes.

So far as we know, the absorption spectrum of benzidine vapours has been investigated only by Pervis([1]). Marsh, McVicker and Stewart([24]) observed Tesla-luminescence. At the same time the fluorescence of benzidine has not been observed hitherto. In view of the availability of an intensive fluorescence of benzidine vapours we also investigated the absorption spectrum, taking care to provide for the most pure experimental conditions possible.

Benzidine (a base) was repeatedly purified by recrystallization and distillation in vacuo. Upon such cleaning, benzidine was found to be non-coloured. For obtaining the absorption spectrum of its vapour a small amount of benzidine thus distilled in vacuo was sealed in an evacuated quartz vessel with a length of 56 mm. In the capacity of source for producing a continuous ultra-violet radiation, a hydrogen discharge tube was made use of. The general set-up for the experiment was the same as is usual for experiments on vapour absorption.

The fluorescence was observed both in the sealed off evacuated vessel containing a small amount of pure benzidine and also in the quartz vessel connected to the vacum set. In this case an ampulla with the substance under investigation was placed into the quartz vessel. Two electric furnaces were mounted on the vessel, owing to which it was possible to vary independently the pressure and temperature.

Condensed sparks jumping the gap between different electrodes (Mg, Al, Zn and Fe) were used as the source of excitation.

D i s c u s s i o n o f R e s u l t s. a) The ultra-violet absorption spectrum of benzidine vapour consists of two regions (Fig. 1). With vapour densities corresponding to 200—250° C the long wave length region of absorption lies within the limits of λ= =3100—2450 Å, having a maximum at λ=2650 Å; the short wave region begins from approximately λ=2300 Å. With an increase in the pressure of the vapours both regions of absorption coalesce into a single broad band of absorption, the long wave boundary of the absorption band being displaced in the direction of long wave lengths. Absorption in both regions proceeded continuously, being deprived of any kind of structure. The absorption spectrum of the vapours is similar to the absorption spectrum of an alcohol solution with the only difference that the latter is displaced in the direction of long wave lengths by approximately 150—200Å ([1,8,9]).

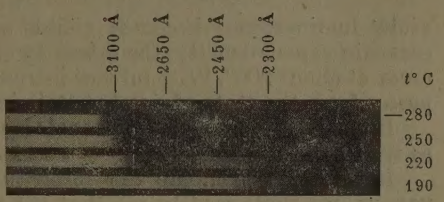

Fig. 1. Absorption spectrum of benzidine vapours at various elasticities (Füss' spectrograph f:5).

Pervis did not succeed in investigating the absorption spectrum of benzidine vapours at temperatures exceeding 172°, as the substance assumed a dark colour which marked the advent of chemical changes. According to Pervis, a thermal decomposition of benzidine took place in this case. Though benzidine is indeed decomposed when heated, it should nevertheless be remarked that the alteration noticed by that author is to be accounted for by the presence of foreign substances in the form of contaminations and can in particular be ascribed to air (oxidation possible), since under the condition of good vacuum benzidine vapours can undergo heating up to 350° without any appreciable alterations.

All at the same time, benzidine is liable to be slowly decomposed with the formation of ammonia, which fact is brought out most forcibly from an

examination of the absorption spectrum. If benzidine vapours be heated during four hours at a temperature of 200°, then within the short wave length region of the absorption spectrum clearly visible bands will be observable which, within the limits of experimental error, will coincide with the bands of ammonia ([10–14]). Thus, beginning from 200° benzidine is slowly decomposed into ammonia and another complex compound, owing to the availability of which the content of the quartz vessel assumes a slightly yellowish hue.

b) Benzidine vapours fluoresce with a bluish-violet light. The region of excitation of fluorescence coincides with that of absorption. If benzidine vapours be excited with the aggregate light of a magnesium, iron, zinc or aluminium spark, it will be clearly seen that the most intensive fluorescence is called forth by the light of the magnesium spark. According to the excitation of fluorescence, the sparks can be ranged in the following order: Mg—10, Fe—6, Zn—3 and Al—1 (the evaluation is made in arbitrary units). In the case of magnesium, fluorescence is on the whole due to excitation by group of intense lines of 2803, 2798, 2796, 2791 and 2780 Å.

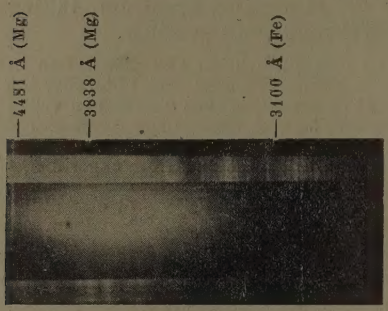

Fig. 2. Fluorescence spectrum of benzidine vapours (Füss' spectrograph $f:5$, vapour temperature 200°, exposure 50 min., spark—Mg).

The fluorescence spectrum represents a single intensive unbroken band in the region of 2950—4500 Å (Fig. 2) with its maximum at 3700 Å. The violet luminescence becomes visible at a temperature above 120°. With increase in vapour density, the intensity of fluorescence rises attaining its maximum at about 200°. With further increase in vapour density, the luminescence passes from the state of a volumetric into the state of a surface phenomenon.

Intensive fluorescence of benzidine is noticeable in an alcohol solution as well as in the solid state.

If we are to compare the absorption spectra of diphenyl and benzidine vapour, we shall readily see that the region of the absorption of the latter (3100—2450 Å) is greatly shifted towards the region of long wave lengths (by approximately 4500 cm^{-1}). Such a considerable displacement of the absorption region is characteristic for the amino-derivative of benzene. Thus, for instance, in the case of aniline the absorption region is displaced relatively to the absorption region of benzene by 4590 cm^{-1} ([15–18]). The existence of thoroughgoing absorption of benzidine in the region of 3100—2450 Å appears quite natural, inasmuch as the absorption spectrum of diphenyl vapour is already continuous. And it is clear that the influence of substitutes—NH_2 can exert any effect only upon the position of the absorption region, as is indeed the case.

From the investigations accomplished by a number of authors([3,6]) and, in particular, from the works by Kato and Someno([7]) it is known that in the absorption spectra of quite a number of amino-derivatives of benzene, apart from the phenyl group there is to be found a second discrete region of absorption with short wave lengths depending upon electronic transition in the substituent. In the case of benzidine it was not found possible to observe structure in the region shorter than 2350 Å (except for the band of ammonia). The reason for this fact is not clear.

Either the NH_2 groups are specially more closely located, which fact involves the mutual influence of identical groups of atoms, or else, the experimen-

tal conditions were unsuitable. In the light of available chemical data various patterns were suggested for diphenyl and its derivatives, namely: the extended one, the curved one and finally the bent one adopted by Kaufler:

. Analysis of the crystal structure ([19]) as well as measurements of the electrical moment ([20–23]) show that for diphenyl and its $p-p'$-derivative the extended pattern has to be assumed ($H_2N-C_6H_4-C_6H_4-NH_2$), seeing that their dipole moment is equal to zero. Therefore we have but to surmise that the experimental conditions, namely: the small thickness of the absorbing layer (56 mm) and the high temperature of vapours necessary for obtaining a sufficient vapour density, were unfavourable for the detection of discrete absorption for the amino-group. Just as is the case for other compounds of the aromatic series, the regions of absorption and emission of benzidine partly overlap.

A most interesting point is that the emission of vapours of diphenyl([24]) falls in respect of its intensity considerably short of the fluorescence of benzidine. In comparing the fluorescence of the vapours of benzol and aniline, a similar phenomenon is observable. This circumstance is undoubtedly connected with the higher coefficient of absorption of benzidine and aniline (approximately 5 to 10 fold), as compared with the coefficient of absorption of diphenyl and benzene.

The continuous appearance of the spectrum of benzidine fluorescence will be easily understood if we bear in mind that the spectrum for the emission of diphenyl vapours is already continuous and contains but a few weak diffuse maxima([24]); this testifies to the strongly disturbing influence of groups of identical atoms.

McVicker, Marsh and Stewart observed the spectrum of Tesla-luminescence of benzidine vapours in the form of an intensive continuous band ranging from 3200—4600 Å (the maximum lying at 3830 Å) ([25]). Consequently, the fluorescence spectrum and the spectrum of Tesla-luminescence are perfectly identical.

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PHYSICS

ON THE POSSIBILITY OF THE FORMATION OF α-RADIOACTIVE NUCLEI IN THE DECAY OF RADIOCHLORINE

By N. N. DMITRIEV, K. A. PETRŽAK and N. A. PERFILOV

(Communicated by A. G. Khlopin, Member of the Academy, 7. IV. 1939)

Libby, Peterson and Latimer(1) claim to have discovered α-radioactivity in argon A^{38} formed from radiochlorine. They gave for that process the following reactions:

1) $Cl^{37} + n^1 \rightarrow Cl^{38}$
2) $Cl^{38} \rightarrow \bar{\beta} + A^{38}$
3) $A^{38} \rightarrow He^4 + S^{34}$ (stable)

The question of the existence of reaction(3) is of paramount importance as a matter of principle. In the first place we have here a new type of nuclear reaction, since no α-radioactive elements have so far been discovered in that section of the periodic system. In the second place, if reaction(3) does exist, this means that A^{38} can exist as two isomers, one of which is a stable (A^{38} is known as a stable isotope, its amount being 0.06%), and the other—α-radioactive one. No such form of nuclear isomerism had so far been discovered. Finally, if in addition to stable A^{38} nuclei, reaction(2) gives rise to α-radioactive ones, there should exist two distinct groups of electrons to correspond to those two possible branches of the reaction. These two groups of neutrons might be identified with the two groups obtained by Kurie, Richardson and Paxton(2), from an analysis of the β-spectrum of radiochlorine. Thus, in the particular case of radiochlorine the «complex» β-spectrum obtained by those writers might be accounted for by the existence of reaction(3).

Subsequently to Libby, Peterson and Latimer, the question of the existence of reaction(3) was dealt with by Roaf(3) who did not succeed in discovering reaction(3). His results cannot, however, be considered as conclusive for a number of reasons. For one thing, Roaf irradiated chlorine with slow neutrons only, while Libby, Peterson and Latimer observed their α-particles upon irradiation of chlorine by fast neutrons. The calculations made by the writers have shown that, from considerations of energy, reaction(3) is undoubtedly possible for fast neutrons ($E \geqslant 4$ MeV). A similar computation for slow neutrons yields no result, since the mass differences obtained prove to be less than the errors in the values of the masses.

We made a number of experiments both with a Wynn-Williams counter, as described in a previous work(4), and with a low pressure Wilson chamber, in order to ascertain whether the decay of radioactive atoms, and, more

particularly, whether reaction (3) does take place. The source of neutrons used had an intensity of about 1100 Mc (nearly six times that of the one used by Roaf). The chlorine was irradiated both by slow and fast neutrons. To slow down the neutrons, a paraffin block (25 cm diam., height 30 cm) was used. The measurements of the irradiated chlorine alternated with those of the background (non-irradiated chlorine). In the first set of experiments, NaCl was irradiated for an hour, whereafter chlorine was separated therefrom; the latter was used to fill the ionizing chamber (capacity 120 cm^3) of the Wynn-Williams counter. The count of the α-particles began five minutes after the end of the irradiation. Under these conditions the counter failed to record any deflections in addition to those of the background for any of the 15 NaCl samples tested, the background being on an average 6 deflections per minute with very sharp tuning (amplification$\sim 10^6$)*. These experiments show no α-radioactivity to be connected with the 37 min. period.

It might have been supposed that α-radioactive atoms could be formed in the decay of some unknown chlorine with a very short period. In order to test that hypothesis, we slightly modified our procedure in such a manner as to be able to utilize the first five minutes after the end of the irradiation. For that purpose the chamber was filled with chlorine from a balloon, the chlorine being irradiated while in the chamber. Irradiation lasted from 5 to 30 min., whereafter the source was rapidly removed and the count of the α-particles was started a few seconds after the end of irradiation. Also in this case, the counter failed to record any additional deflections not accounted for by the background. These experiments have shown that no α-radioactivity is connected with the short period of chlorine (if such be assumed to exist at all). As shown by these experiments, the effective section for the ejection of α-particles from chlorine due to neutrons is $\sigma < 10^{-27}$ cm^2.

Since our Wynn-Williams counter could be fully relied upon to record only the α-particles having a path of 2 mm and over, we made a number of experiments with a low pressure Wilson chamber (diam. 26 cm) in order to ascertain whether any α-particles having a path of less than 2 mm were ejected. The liquid used to produce saturation was ethyl alcohol. The chlorine was admitted into the chamber as chloroform vapour (the total initial pressure being 13 cm Hg). Exposures of 10—15 min. were used, the count of the heavy particle paths beginning 5—8 sec. upon irradiation. To eliminate individual errors two experimenters counted independently the number of heavy particle paths below 4 cm arisen in a definite number of expansions. The background consisted on an average of 27 heavy particles per 200 expansions (4 min.). No additional effect not accountable for by the background was discovered.

In another set of experiments, the target placed within the chamber was a copper plate (18 cm long, 1 cm wide) coated with copper chlorides. Count was taken of the total number of heavy particles escaping from the plate on both sides of it. In these experiments, the background was on an average 12 heavy particles per 300 expansions. These experiments also failed to reveal any additional effect not accounted for by the background. The experiments carried out with the Wilson chamber have shown that radiochlorine does not give rise to α-particles having a path below 2 mm.

The results obtained suggest the following conclusions:

1) No α-radioactivity would appear to be produced by radiochlorine, since the argon formed in the decay of radiochlorine is stable.

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* Taking for a standard the magnitude of the effect given by Libby, Peterson and Latimer, the number of deflections that we ought to have observed under our conditions was about 15 in addition to the background.

2) Considered from the point of view of nuclear isomerism this would mean that stable argon had no α-radioactive isomer. Consequently, the question as to the possibility of a real existence of such a form of isomerism as is characterized by α-decay of one isomer and stability of the other still remains open.

3) Should a further investigation of the β-spectrum of radiochlorine confirm the existence of two groups of electrons, such a «double» β-spectrum could not be accounted for by the α-radioactivity of a part of argon atoms and could only be due to some other case.

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PHYSICS

ON THE VOICE OF THE SEA

By N. N. ANDREEV, Corresponding Member of the Academy

Prof. Shoulejkin explains the voice of the sea discovered by him (1)—i. e. infra-sound vibrations emanating from the sea's surface—by the assumption that these vibrations are occasioned by the wind impinging against the crests of waves. Here is a quotation from Prof. Shoulejkin's paper (2): «In air, as in a medium which can be easily compressed, density fluctuations are liable to be set up, being caused by the periodic encounters of the wind with the crests of waves. If we assume the distance between these crests as being equal to approximately 1 m and if the wind velocity be taken of the order of 10 m/sec., then, one and the same mass of air will on its way encounter the summits of „water hills" approximately every tenth part of a second. Thereby longitudinal infra-sound waves with a frequency of the order of 10 Hz will be set up in air».

In this explanation a physical picture of sound formation appears to be lacking, wherefore the account given by the author seems to be rather indefinite. But the explanation, if taken in the above-quoted wording, may furthermore easily be found to contain a certain internal contradiction (i. e. if we attempt to decipher the indefiniteness of the statement). Indeed, it would seem that Prof. Shoulejkin imagines things in such a way as if the periodicity of sound were set up by the number of crests encountered by wind on its way. But this can be unterstood only if we consider matters from the point of view of an observer who would be moving with wind. As to an observer who would be standing on the shore, for him frequency is determined by the number of vibrations at the spot where the sound is formed, and it stands to reason that at the given spot in the middle of the sea this number will not depend upon the velocity of wind relatively to the velocity of waves, but solely upon the velocity of waves. Now, wind velocity is capable of influencing only the amplitude of the voice of the sea*. But the frequency observed in this case would be that of sea waves, i. e. it would be of the order of 1 m. From a communication of Shoulejkin, which he was kind enough to make me, I know that he observed such frequencies too, but it is not of them he speaks in his account, but only of frequencies of the order of 10 Hz.

The order of power of these waves has been calculated by Shoulejkin on the basis of Jeffrys's calculations** who had in view to find a criterion

* Indeed, since the equations for the acoustics of a moving medium differ from ordinary ones, yet they are linear and the solution has a factor $e^{j\omega t}$, ω being determined by boundary vibrations. There will be in our case no mutual transposition of source and observer involving the application of Doppler's principle.

** Physics of the Sea, II, p. 84—85.

for the formation of waves by wind. But it should be borne in mind that in Jeffrys's calculations we deal not with impacts, but with the mean force of the friction of wind against the sea surface which with sufficient velocity involves a breach in the stability of small surface vibrations.

In connexion with this the following considerations might be of interest.

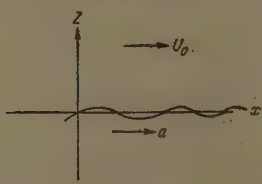
First of all let us consider the voice of the sea estimated by Shoulejkin at 10 Hz. If this cannot be explained through the steady flow of wind along the surface of waves, the surmise can readily be made to the effect that this voice is caused by turbulent motion in course of the streamline flow of wind around wave crests. The formation of periodical turbulences beyond an impediment with constant streamline motion around this impediment has been known long since and has been thouroughly investigated for many cases, e. g. for a cylinder and plate (3). In this case the frequency of the sound formed is governed by the dimensionless relationship:

$$\frac{ND}{U} = f\left(\frac{UD}{\nu}\right) \qquad (1)$$

which was given by Lord Rayleigh. Here U is velocity of wind relatively to cylinder, D — diameter of cylinder, N — frequency of curls formation, ν — air viscosity, $\frac{UD}{\nu} = R$ — Reynold's number. This formula has good evidential support (3). In our case it is possible to take for D the height of a wave coming, say, to 100 cm. Let us assume U as equal to $3 \cdot 10^3$ cm/sec. Finally f depends but little upon R and for a cylinder experimental evidence gives $f \sim 0.2$ (3). Hence we have

$$N = \frac{0.2 \cdot 3.10^3}{10^2} = 6\text{Hz},$$

i. e. we obtain an order of magnitude which is close to the one we are envisaging. With all the roughness of this calculation (from a cylinder to the sinusoidal surface of the sea!) it nevertheless shows that the origin of the „voice of the sea" can, with great plausibility, be ascribed to the periodical formation of curls. At any rate, this problem deserves the most careful investigation. It would be interesting to study sound-formation due to turbulences on a model of the sea—a big cylinder rotating in air, with an undulating surface. From experiments with such a cylinder it would be possible to determine f (R) in dimensionless formula (1), and then f; the basis of wind velocities and wave periods observed, it would be possible to calculate the frequencies of the possible „voices of the sea".



But besides curls-formation, infra-sound vibrations in air may also be due to vibrations of sea waves at the boundary of air. If, in the first approximation, we assume small vibrations and certain other simplifying relationships mentioned below, we may perform a rough calculation of the phenomenon under consideration.

Let us assume that we are dealing with bidimensional waves of sinusoidal type. Consequently, at the lower boundary of air with $z=0$ (figure) we have:

$$v_z = w_0 e^{j\omega\left(t-\frac{x}{a}\right)}, \qquad (2)$$

where a is velocity of propagation of sea waves in direction x, ω is their frequency and w_0 ist the amplitude of their velocity. Concomitantly with

this boundary condition it is necessary to find the sound potential of air which, as the writer has shown before ([4]), satisfies the following system of equations:

$$\frac{\partial^2\varphi}{\partial t^2}+2u_0\frac{\partial^2\varphi}{\partial x\partial t}+u_0^2\frac{\partial^2\varphi}{\partial x^2}=c_0^2\left(\frac{\partial^2\varphi}{\partial x^2}+\frac{\partial^2\varphi}{\partial z^2}\right); \tag{3}$$

$$p=\rho_0\left(\frac{\partial\varphi}{\partial t}+u_0\frac{\partial\varphi}{\partial x}\right). \tag{4}$$

$$v_x=-\frac{\partial\varphi}{\partial x};\ v_z=\frac{\partial\varphi}{\partial z}, \tag{5}$$

u_0 being velocity of wind, assumed to be directed along the axis of x's and being equal at all heights; c_0 is velocity of plane sound waves in quiescent air.

The most suitable particular integral for our purpose is:

$$\varphi=\varphi_0 e^{j\omega\left(t-\frac{\alpha x+\gamma z}{c_1}\right)} \tag{6}$$

whose substitution into equation (3) and boundary condition (2) gives us φ_0, α, γ, c_1. In result we find

$$\varphi=\varphi_0 e^{-\delta z+j\omega\left(t-\frac{x}{a}\right)} \tag{7}$$

where

$$\delta=\frac{\omega}{a}\sqrt{1-\left(\frac{u_0}{c_0}-\frac{a}{c_0}\right)^2}, \tag{8}$$

$$\varphi_0=-w_0\frac{a}{\omega\sqrt{1-\left(\frac{u_0-a}{c_0}\right)^2}}, \tag{9}$$

$$p=j\omega\rho_0\varphi\left(1-\frac{u_0}{a}\right). \tag{10}$$

Thus, as could be expected, we find the availability of a surface wave in air with an amplitude of pressure

$$|p|=\frac{w\,(u_0-a)\,c_0}{\sqrt{c_0^2-(u_0-a)^2}}e^{-\delta z}. \tag{11}$$

Consequently, the force of sound is proportional to $w_0^2=(\xi_0\omega)^2$ (ξ_0 is amplitude of wave) and almost proportional to $(u_0-a)^2$, declining with altitude above sea level. It is necessary to note that — as is always the case for surface waves — their velocity is less than the velocity of sound and equals in our case the velocity of a, i. e. is of the order of 30 m/sec.

As sea waves have great amplitudes with a frequency of 1 Hz, it becomes probable that the «voice of the sea» of such frequency is brought about by our surface waves. It would be interesting by means of experiments conducted from on board ship in the zone of a rough sea to trace the exponential dependence $e^{-\delta z}$ with altitude. In the case of wind increasing with altitude our calculations are no longer applicable, and neither are they so in the case of turbulent wind; but the general character of the phenomenon is retained in these cases too. It can be expected that δ increases with the availability of gradient.

Our calculation is valid only for a zone of rough seas. Outside its limits the sound energy of air caused by the heavy seas is propagated in different directions and proceeds with ordinary sound velocity, being damped down with distance.

Assuming $\xi_0=100$ cm and $\omega=2\pi$, we find, with $(u_0-a)=3\cdot10^3$, pressure $|p|$ in dynes to be approximately equal to $2\cdot10^6$ dynes, which explains

the greater sound power of waves (this is for the zone of rough sea; further on it decreases, roughly speaking, in accordance with the law of squares).

Despite the approximative character of our calculation, it yet seems to be of interest, since, on the one hand, it points to the existence of sound-formation processes of the type of surface waves, while, on the other hand, it makes an attempt at presenting a clear physical picture of this sound-formation process.

Anyway, besides its infra-sound voice, the sea has also a number of other „voices" and this not only in the field of audible frequencies (the sound of surf, the sound of pebbles being moved by waves, etc.), but also ultra-sound frequencies. The latter, in distinction to the first two, were observed only under water by Langevin and Marcelin and are the own high-frequency vibrations of small pebblestones carried and dropped by the sea.

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PHYSIK

MESSUNGEN DER FORTPFLANZUNGSGESCHWINDIGKEIT DER ELEKTROMAGNETISCHEN WELLE LÄNGS EINER DOPPELLEITUNG IN UNHOMOGENEM MEDIUM

Von N. N. MALOV

(Vorgelegt von S. I. Wawilow, Mitglied d. Akademie, d. 9. IV. 1939)

Bei der Untersuchung der elektrischen Eigenschaften der Flüssigkeiten nach der ersten Drude'schen Methode (Fortpflanzung der Welle längs einer Doppelleitung) nimmt man an, dass die Flüssigkeitsgrenzen unendlich weit entfernt sind.

Um die Frage zu erklären, wie gross der Einfluss der endlichen Entfernung der Flüssigkeitsgrenzen auf die Geschwindigkeit der Welle sein kann, wurden folgende Experimente unternommen.

In ein Glassgefäss mit der Flüssigkeit (Wasser, die Leitfähigkeit $g<10^{-4}$ prakt. Einh., $t=15$—$17°$ C) wurde eine horizontale Doppelleitung eingeführt (Abb. 1, rechts). Längs der Leitung konnte man eine Brücke (Durchmesser 70 mm) mittels der Mikrometerschraube verschieben. Ein Spannungsindikator stand vor dem Gefäss in einem Spannungsbauch.

Die Doppelleitung wurde mittels Magnetrongenerator erregt (Wellenlänge in der Luft ca. 65 cm); die Kopplung war induktiv und sehr schwach gewählt.

Die Wellenlänge war in der Flüssigkeit bei verschiedenen Dicken der Schichte h (über der Leitung) gemessen. Die untere Kurve der Abb. 1 zeigt, dass bei $h \geqslant 30$ mm die Wellenlänge von der Dicke h unabhängig ist.

Bei kleineren Dicken nimmt die Wellenlänge zu (die Punkte für $h=24$ mm fallen aus der Kurve). Es ist von Interesse, dass die Grösse der weiten Spannungsmaxima (bei kleinen h-Werten) die nahe Maxima überschreiten kann (die obere Kurve, Abb. 1), was man bei grossen h-Werten niemals beobachtet.

Die Ergebnisse dieser Messungen sind in Abb. 2 (*K*urve *I*) dargestellt; λ bedeutet die Wellenlänge bei gegebener h, $\frac{\lambda}{\lambda_\infty}$ — bei $h>30$ mm).

Die Änderungen des Durchmessers der Doppelleitung (1 und 2 mm) und der Grösse der Brücke (35×35 und 90×120 mm^2) übten keinen merklichen Einfluss aus.

In einer wässrigen NaCl-Lösung ($g=1.1\cdot10^{-2}$ prakt. Einh.) war eine kleinere Zunahme der Geschwindigkeit gemessen $\left[\left(\frac{\lambda}{\lambda_{\infty\,\max}}\right)=1.28\right]$.

Man könnte erwarten, dass der Einfluss der Dicke h im Falle einer vertikalen Doppelleitung kleiner würde (die Dicke h wird von der oberen Leitung abgezählt)! Die Messungen bestätigten diese Erwartung, wie die Kurve *II* der Abb. 2 zeigt.

Auch im Falle alleinstehender Leitung wurde ähnlicher Einfluss der Dicke h beobachtet. Leider waren in diesem Falle genaue Messungen der Wellenlänge unmöglich, da die Resonanzkurven ziehmlich unklar waren.

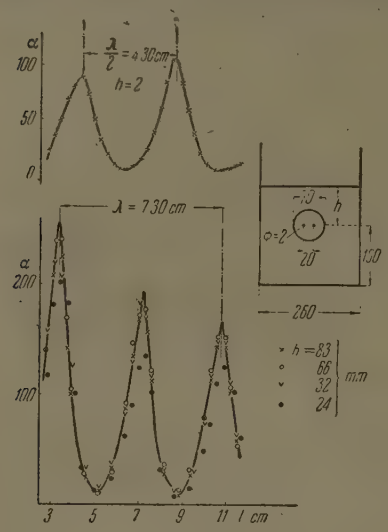

Fig. 1.

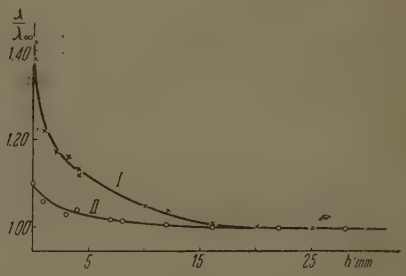

Fig. 2.

Bei negativen h-Werten (die Flüssigkeitsgrenze liegt unter der Leitung) konnte man die Wellenlänge nicht messen, da die Länge der Schraube zu klein war (20 cm).

Da die Rechnung der Geschwindigkeit in allen diesen Fällen sehr schwierig ist, können schon diese orientierende Daten von Bedeutung sein (z. B. bei elektromagnetischen Messmethoden der Entfernungen).

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TECHNICAL PHYSICS

PICTURE OF REFLECTION AND ITS APPLICATION IN ARCHITECTURAL ACOUSTICS

By G. A. CHIGRINSKY

(Communicated by A. F. Joffe, Member of the Academy, 17.III.1939)

1. 1. The path of a ray repeatedly reflected from the faces of a rectangular parallelepiped may be represented by its unfolded image in two or three projections upon planes parallel to the faces of the parallelepiped.

In each of the projections the images of the points of reflection of the ray are disposed at the points of intersection of the direction of this ray with the sides of a „reflection network", the meshes of this network being equal to that face of the parallelepiped which is parallel to the plane of the respective projection (Fig. 1. 1).

The points of intersection of the ray with the sides of the reflection network in any of the planes, say in the horizontal plane Γ (1, 4, 7, 9, 12, 15), represent the images of the points of reflection of the ray from the faces of the parallelepiped which are at right angles to this plane.

The image of the ray plotted on a reflection network will be hereinafter called the „picture of reflection" (P. R.). The picture of reflection permits to find the points of intersection of the rays with any given section on the face of the parallelepiped (section F in Fig. 1. 1).

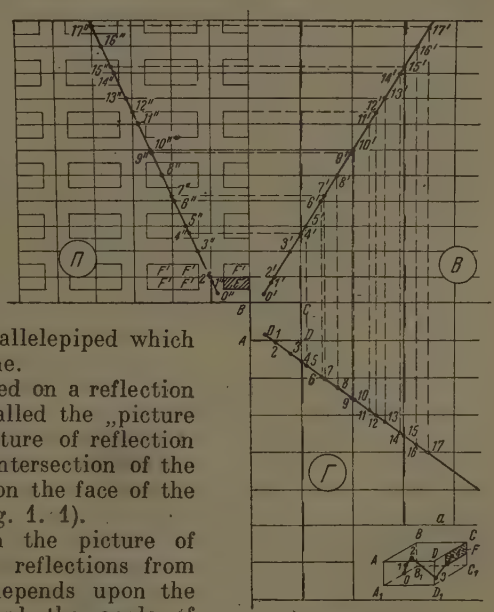

Fig. 1.

1.2. It may be seen from the picture of reflections that the number of reflections from each pair of parallel faces depends upon the distance between the faces and the angle of incidence of the ray and does not depend on the disposition of the faces which are perpendicular to the said first pair.

The total number N of the reflections of a ray along the path L is the sum of the numbers n_1, n_2 and n_3 of its reflections from each pair of parallel faces of the parallelepiped with the length of the sides a, b and h.

$$N = n_1 + n_2 + n_3 = \left|\frac{L\cos\alpha\cos\gamma}{a}\right| + \left|\frac{L\cos\alpha\sin\gamma}{b}\right| + \left|\frac{L\sin\alpha}{h}\right|. \qquad (1.1)$$

The mean free path of a ray between the points of reflection is equal to

$$\lambda = \frac{L}{N} = \frac{1}{\left|\frac{\cos\alpha\cos\gamma}{a}\right| + \left|\frac{\cos\alpha\sin\gamma}{b}\right| + \left|\frac{\sin\alpha}{h}\right|}, \qquad (1.2)$$

where γ is the azimuth which is reckoned from the side a and α is declination which is reckoned from the plane ab.

The items of the denominator of the expression (1.2) ought to be taken in their absolute value.

1.3. With the aid of the picture of reflection the following problems connected with the reverberation of various rooms may be solved: a) The effect of the shape of the room (its dimensional proportions) on the reverberation. b) The effect of the disposition and distribution of sound absorbing materials and of openings in the boundary walls on the reverberation. c) The effect of the directional characteristics of the source of sound upon the reverberation. d) The reverberation in partly open rooms.

1.4. The energy of sound within a room at a time t seconds after the emission of sound by the source has ceased is determined as follows.

Let us find for each ray on the length of path $L=ct$ the number of reflections and the coefficients of reflection β at the points of reflection.

The initial energy being I_0, the energy I_1 in the instant t is:

$$I_1 = \frac{I_0}{K}\sum_{i=1}^{i=k} \beta_1^{l_i}\ \beta_2^{m_i}\ \beta_3^{p_i} \qquad (1.3)$$

where K is the number of rays in the picture of reflection, l_i, m_i, p_i are the numbers of intersections of a ray with the surfaces having identical reflecting coefficients.

If we know the magnitudes of the decay of the energy for consecutive instants of time, we can find the standard reverberation time, account being taken of the factors enumerated in 1.3. The directional ability of the source is defined as the density of rays intersecting separate portions of the spherical surface described about the source as a center.

2. Reverberation in an Unclosed Space. 2.1. Let us consider two cases of an unclosed room:

1) A parallelepiped destitute of one or two parallel faces.

2) Three planes, two of which are parallel.

The picture of reflection for a room bounded by five faces of a parallelepiped $AA'BB'CC'DD'$, in which the face $AA'DD'$ is missing, is shown in Fig. 2.1. The rays of sound from the source K after their reflection from the existing faces will pass through the open faces $AA'DD'$ without being reflected. In the case under consideration the reverberation time depends upon the mutual position of the source and the point of the perception of sound, whereas in an enclosed room this position is of no importance.

For a point of perception of the sound S the region which creates reverberation will be that of the hatched sections of the sides. The sections laying between the point S and the face $AA'DD'$ send the rays reflected by them into the outside space. The picture of reflection in the planes parallel to $ABDC$ and $AA'BB'$ will be bounded by the lines $m'n'$ and $m''n''$ drawn at a distance AB from the line mn along which the surface $BB'CC'$ is projected upon the picture of reflection.

2.2. Let us lay off along the rays of the picture of reflections a length $L=ct$ (Fig. 2.2). The extremities of this length will be disposed on a spherical zone of the height $2h$ (h being the distance of the point of perception of

sound from the face $BB'CC'$). The amount of energy in a not fully enclosed room after N reflections is:

$$I_1 = A \cdot I_0 (1-\alpha)^N. \tag{2.1}$$

$I_0(1-\alpha)^N$ is the energy in the enclosed room as summarized for all rays of the picture of reflection at their points disposed on the complete surface of the sphere (Fig. 2.2). A is the coefficient of leakage of the energy of sound escaping through the missing face. The value of A is determined from the relation between the flux of energy remaining in the room and the total flux of the source. It is equal (for an undirectional

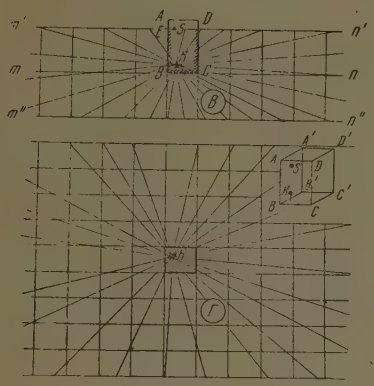

Fig. 2.

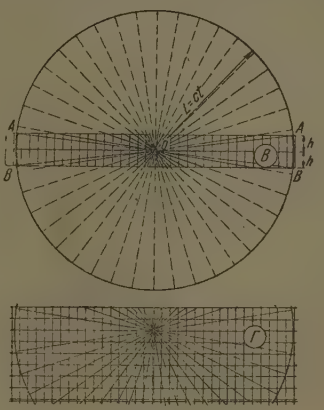

Fig. 3.

source) to the ratio of the area of the spherical zone $AABB$ having a radius ct and a height $2h$ to the area of the spherical surface having the same radius.

$$A = \frac{2\pi r h}{2\pi r^2} = \frac{h}{r} \quad \left(\text{or if } h \text{ is great, } A = \frac{h}{\sqrt{h^2 + r^2}}\right). \tag{2.2}$$

If $r = ct$ and $N = \frac{r}{\lambda} = \frac{ct}{\lambda}$ (where λ is the mean free path of the ray), then the energy of sound in the not fully encompassed room at the instant t is

$$I_1 = I_0 \cdot \frac{h}{ct} (1-\alpha)^{\frac{ct}{\lambda}}. \tag{2.3}$$

In order that the amount of the decay of sound should be 60 decibels we must have

$$\lg \frac{I_0}{I_1} = \lg \frac{c\, t_{60}}{h (1-\alpha)^{\frac{ct}{\lambda}}} = 6,$$

whence we can derive the expression for the reverberation in a not fully enclosed room of the height h:

$$\lg \frac{ct_{60}}{h} - \frac{ct_{60}}{\lambda} \cdot \lg (1-\alpha) = 6. \tag{2.4}$$

The mean free path λ is determined from the picture of reflection.

The above expression implies the existence of the so-called two-dimen-

sional reverberation and gives instead of a straight line a curved line of decay of the sound energy, whereon the sound level is first sinking rapidly and then more slowly to the end of the period of decay.

2.3. For the second case (three planes two of which are parallel) the formula for the time of the reverberation may be derived in an analogous manner:

$$2\lg ct_{60} - \frac{ct_{60}}{\lambda}\lg(1-\alpha) = 5.502 + \lg l, \tag{2.5}$$

where l is the projection of the distance between the source and the sound receiver upon the parallel planes.

3. Octahedron of Sound Isobars. 3.1. Let us find on the picture of reflection the position of the points corresponding to a constant sound level. Let us locate the source of sound in the centre of the parallelepiped and consider three rays at right angles to the three faces.

If the dimensions of the parallelepiped are $a_1 \times a_2 \times a_3$ and the respective reflecting coefficients of the faces normal to the sides are β_1, β_2 and β_3, then the distances L_i from the source to the points with the same sound level on the three rays may be found from the following expressions:

$$I_1 = I_2 = I_3; \quad I_i = I_0 \cdot \beta_i^{\frac{L_i}{\lambda_i}}$$
$$\beta_1^{\frac{L_1}{a_1}} = \beta_2^{\frac{L_2}{a_2}} = \beta_3^{\frac{L_3}{a_3}}. \tag{3.1}$$

(a_1, a_2 and a_3 are the mean free paths of the rays for the chosen directions). Taking logarithms of (3.1) we find:

$$L_1 : L_2 : L_3 = \frac{a_1}{\lg \beta_1} : \frac{a_2}{\lg \beta_2} : \frac{a_3}{\lg \beta_3}. \tag{3.2}$$

3.2. As regards the rays occupying intermediate positions between the three chosen directions intersecting one another at right angles, the values of their mean free paths may be found from the formula (1.2) which for the case under consideration receives the following form:

$$\lambda = \frac{L}{N} = \frac{1}{\left|\frac{\cos\alpha \cdot \cos\gamma}{a_1}\right| + \left|\frac{\cos\alpha \cdot \sin\gamma}{a_2}\right| + \left|\frac{\sin\alpha}{a_3}\right|}. \tag{3.3}$$

For the rays lying in the planes $a_1 - a_2$, $a_2 - a_3$, $a_3 - a_1$ we find respectively:

$$\lambda_1 = \frac{1}{\left|\frac{\cos\gamma}{a_1}\right| + \left|\frac{\sin\gamma}{a_2}\right|}; \quad \lambda_2 = \frac{1}{\left|\frac{\cos\alpha}{a_2}\right| + \left|\frac{\sin\alpha}{a_3}\right|}; \quad \lambda_3 = \frac{1}{\left|\frac{\cos\alpha}{a_1}\right| + \left|\frac{\sin\alpha}{a_3}\right|}. \tag{3.4}$$

If we lay off the lenghts of the mean free paths upon these rays passing through the centre of the parallelepiped, we find that their ends are disposed on straight lines which connect respectively the points A and B, A' and B', A and C, A' and C', C and B, C' and B' (Fig. 3.1). It is easy to see that the extremities of the sections corresponding to the mean free paths of the rays directed outside the above planes lie in the planes ACB and $A'C'B'$, $A'CB$ and $AB'C'$ and so on.

In this manner we have obtained an octahedron, the vertexes of which lie in the centres of the faces of the parallelepiped and the principal diagonals are equal to a_1, a_2 and a_3. We shall call it the octahedron of mean free paths. To find the mean free path of the ray of any direction it is necesssary to draw a secant line through the centre of the octahedron of M. F. P. parallel to the direction of said ray.

3.3. Referring again to the formula (3.2) we see that the lengths L_i corresponding to an equal decay of the sound energy along the ray are pro-

portional to the mean free path of the ray divided by the logarithms of the reflecting coefficients of the corresponding surfaces.

It is obvious that an octahedron having diagonals mutually at right angles which pass through the centres of the faces of the parallelepiped and are equal respectively to

$$\frac{a_1}{-\lg \beta_1}; \qquad \frac{a_2}{-\lg \beta_2}; \qquad \frac{a_3}{-\lg \beta_3}$$

represents the level surface of sound energy for the rays propagated from the centre O of the parallelepiped.

We shall call this surface the octahedron of sound isobars. A family of such surfaces with the diagonal's

$$\frac{ka_1}{-\lg \beta_1}; \qquad \frac{ka_2}{-\lg \beta_2}; \qquad \frac{ka_3}{-\lg \beta_3}$$

gives us a conception of the variations of sound energy in different directions passing through the point O.

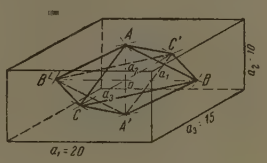

Fig. 4.

3.4. The reverberation time for a directed flux of sound in a room is proportional to the length of a secant line drawn through the centre of the octahedron of sound isobars parallel to the given direction.

By substituting in the formula (3.3) $\frac{a_i}{-\lg \beta_i}$ for a_i we obtain after some necessary transformations the reverberation time of a directed flux (ray) as follows:

$$t_{60} = -\frac{0.0176}{\left|\frac{\cos\alpha\cos\gamma}{a_1}\right| \lg\beta_1 + \left|\frac{\cos\alpha\sin\gamma}{a_2}\right| \lg\beta_2 + \left|\frac{\sin\alpha}{a_3}\right| \lg\beta_3}. \qquad (3.5)$$

3.5. A uniform reverberation in three directions is attained when the reflecting coefficients of the faces of the parallelepiped are determined by the formula

$$\frac{a_1}{\lg\beta_1} = \frac{a_2}{\lg\beta_2} = \frac{a_3}{\lg\beta_3} \qquad (3.6)$$

which corresponds to an octahedron of sound isobars having equal diagonals.

3.6. If identical reflecting coefficients β_a from two parallel surfaces are replaced by two different reflecting coefficients β_b and β_c, we obtain the condition:

$$I_0\beta_a^{\frac{L}{\lambda}} = I_0\beta_b^{\frac{L}{2\lambda}}\beta_c^{\frac{L}{2\lambda}}. \qquad (3.7)$$

Taking the logarithm of this expression we find:

$$\lg\beta_a = \frac{\lg\beta_b + \lg\beta_c}{2}. \qquad (3.8)$$

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CHEMICAL PHYSICS

ON THE THEORY OF THE DEVELOPMENT OF DETONATION IN GASES *

By K. I. SHTSHOLKIN

(Communicated by N. N. Semenov, Member of the Academy, 4. IV. 1939)

It has long been known ([1], [2]) that the detonation of a combustible mixture contained in a tube and ignited by means of an electric spark is preceded by an accelerated propagation of the flame. The present is an attempt to explain the mechanism of this acceleration. The question is quite timely since, in spite of its not being new and of the great practical interest it presents, the theoretical interpretation of the process, and even a more or less satisfactory picture thereof, are still lacking.

Much work has already been done relating to the effect of various factors on the distance of the «position of detonation» ([3–10]) from the spark. However, while measuring these distances, most of the investigators failed to record the time between ignition and detonation. Nothing definite can therefore be said concerning the acceleration of the flame under changing experimental conditions.

In connexion with the problem in hand, we were especially interested in the influence of pressure on the detonation; we therefore measured both the distance from the spark to the position of detonation, and the time between the moment of ignition and that of detonation, using a mixture of $C_5H_{12}+8O_2+3N_2$ contained in a glass tube 175 cm long and 16 mm wide. Some of the results obtained are tabulated below.

Table 1

Initial pressure in mm Hg	Position of detonation (distance L in cm)	Time t in sec.	Ratio L/t in m/sec.
365	66	1.93	342
450	52.8	1.88	431
800	49	1.023	478

With the increase of the initial pressure, the position of detonation is seen to be nearer to the spark. The time interval between ignition and detonation also shortens, so that the ratio L/t increases. This can be explained only by assuming that the increase of the initial pressure causes the acceleration of the flame during the predetonation period. Even if the ratio L/t were independent of pressure, the shortening of the time interval between

* Abstract from the author's Thesis (October 1938).

ignition and detonation would be a convincing proof in itself that as the pressure increases the progress of the flame becomes accelerated. Indeed, in the case of uniformly accelerated motion we have $L/t = \frac{gt}{2}$, whence the increase of the ratio L/t (or its constancy), and the simultaneous decrease of t, can occur only at the expense of an increase of g.

The increase of the acceleration of the flame with the pressure will seem the more surprising, if we consider that the increase of the initial pressure does not in the least affect the normal propagation of the flame ([11], [12]). We are thus led to assume that the acceleration of the flame prior to detonation is due not to changes in the velocity of the n o r m a l propagation of the flame, but to other causes.

Other examples can be quoted where the development of the detonation is favoured by physical factors which do not in the least affect the velocity of the normal propagation of the flame (or fundamental velocity). Laffitte ([6]), for instance, found that in a tube lined with sand ($d = 1—3$ mm), other conditions being equal, the detonation started at a point much nearer to the spark. In the course of our experiments we also were able to ascertain the rôle of rough and uneven walls in the development of detonation. In the case of rough walls the limiting pressure at which spark-ignited detonation is still possible also decreases ([13]).

In view of the above, the cause of the acceleration of the flame during the predetonation period must be sought in the turbulence of the gas stream (due to the expansion of the burning gases) in front of the propagating flame. When the stream becomes turbulent, the propagation of the flame alters markedly.

Owing to the pulsations, the stream of burning gases will mix with the fresh supply of gas. The front of the flame becomes jagged, its surface extends considerably and the linear velocity of propagation also increases. In front of the accelerated flame Payman and Titman ([14]) have observed compression waves which, overtaking one another, unite in a powerful shock wave causing detonation. There still remain some obscure details, and the proposed mechanism requires further improvement; still, on the whole, the hypothesis can be said to explain quite satisfactorily all the observed experimental facts. Increased pressure and rough walls favour the development of turbulent motion in the gas, and therefore the acceleration of the flame, thus facilitating the start of the detonation. From this stand-point the effect of other factors can also be easily explained. However, general considerations may not be convincing enough; it is only a quantitative agreement between computed and experimental values which can decide in favour of one or another theory or hypothesis. We therefore intend to give the results of a few calculations based on the above theory.

It follows from the above that when the concentrations of the combustible gas reach definite values at which ignition by spark or flame ceases to initiate detonation (at the so-called «explosion limits»), the Reynolds numbers referred to the stream of the fresh gas in front of the flame at its start pass through a critical value. Outside these concentrations where the detonation fails to occur, the value of the Reynolds numbers are below the critical value, while within these concentrations they exceed it.

To a first approximation, the velocity of the fresh gas in the vicinity of the flame front is of the same order of magnitude as that of the flame. The relative error involved is about $\frac{T_0 n_0}{T_1 n_1}$; T_0 and T_1 being the initial temperature and that of the flame respectively, n_0 and n_1, the number of moles before and after combustion. To a rough approximation, the Reynolds criterion

can be represented in the form $Re = \frac{rv}{\nu}$, where r is the radius of the tube, ν—the kinematic viscosity and v—the velocity of the flame with respect to the gas prior to its acceleration. This velocity will be replaced by the better known and more reliable value of the normal (fundamental) velocity of the flame propagation, and the required correction will then be applied.

Table 2 gives the Reynolds numbers calculated in this way for concentrations of the combustible, below and above which spark ignition no longer initiates detonation. The table includes all the substances for which experimental figures for both the limiting concentration and the corresponding normal velocity of propagation are available simultaneously.

Table 2

Mixture	Limiting concentration in % of combustible	Reference	Velocity of normal flame propagation in cm/sec.	Reference	$Re = \frac{\delta r v}{\eta}$
H_2 + air	28 35.5	13	200 270	18	1150 1430
H_2 + oxygen	23 85	13	180 440	18	1070 1150
C_2H_2 + air	6.5 15	15	100 60	19	680 420
CO + oxygen	60 72	16	95 100	17	640 670
CH_4 + oxygen . . .	10 60	16	240 —	20	1600 —

The figures for the viscosity are given in Table 3.

Table 3

Substance	$\eta \cdot 10^7$	Substance	$\eta \cdot 10^7$
Air	1820	O_2	2010
H_2	870	CH_4	1080
C_3H_2	1000	CO	1740

The viscosity of a mixture was computed from the viscosities of its constituents. The velocity of propagation corresponding to the limiting concentration was determined graphically, by interpolating the known experimental values. The high value of Re for methane, as compared with other gases, can be explained by the fact that in this case the calculation was based on the velocity of uniform movement which somewhat exceeds the normal velocity. For this mixture the value of Re for the upper limit could not be determined, since the value of the corresponding velocity is not sufficiently reliable [thus, according to Rivin and Sokolik ([16]), a mixture of oxygen and 60% methane does detonate, while Payman ([20]) declares that in such a mixture the flame does not propagate at all].

If we consider that the velocity of the flame in the tube constitutes about the double of the fundamental (normal) velocity, then the calculated values of Re will rise to some 1300—2300, slightly beyond the critical values ($Re_{cr} \approx$ $\approx$1000—1100). Outside the limiting concentration Re lies below the critical value, within it—is considerably higher, attaining values of tens of thousands. These results can be considered to be quite satisfactory and to support the advanced hypothesis, especially since the various experimental data used for its test have been obtained by different investigators.

Apart from the calculation of Re corresponding to the limiting concentrations, the minimum pressure can be calculated at which the detonation still arises in tubes filled with different gas mixtures. With decreasing pressure the value of Re also decreases owing to the decrease in density. Finally, the value of Re attains the critical value. The pressure at which the value of Re falls below the critical value, is the minimum pressure at which detonation sets in spontaneously in a mixture ignited by a weak agent (spark, flame).

Table 4 contains the experimental data for the minimum pressure in oxygen mixtures of CH_4 ([16],[20]) and of H_2 ([18],[21]), as well as the corresponding values computed with the aid of the theoretical expression

$$P = Re_{cr} \frac{760\eta}{v r \delta_0} \text{ mm Hg},$$

deduced on the basis of the above considerations. Here v is the velocity of the flame propagation in tubes which, as already said, for a number of mixtures proves to be independent of the pressure. It was assumed that this independence from pressure will hold for oxygen mixtures of CH_4 and of H_2. In these calculations, instead of the normal velocities, the velocity of flame propagation in tubes was used, since for this the variations with the concentration are better known ([20], [21]).

Table 4

CH_4 + oxygen			H_2 + oxygen		
% CH_4	P_{min} calc. in mm Hg	P_{min} obs. in mm Hg	% H_2	P_{min} calc. in mm Hg	P_{min} obs. in mm Hg
10	760	760	23	760	760
15.5	253	213	24.2	678	678
21.6	80	70	29.5	488	312
27	46	57	33.8	372	250
33	33	70	39.2	282	205
40	61	114	48.5	215	143
45.6	381	187	52.6	198	113
53.4	2270	400	77.5	328	300
—	—	—	80	487	400
—	—	—	81.6	600	510

The value of Re_{cr} was calculated for the lower limit of concentration at atmospheric pressure; δ is the density at 760° mm Hg and 17° C, r=1 cm, η is the viscosity (Table 3).

As before, at the upper limit, the calculated and observed values for methane show a marked discrepancy, the reason of which has been pointed out above.

On the whole, the agreement between the calculated and observed values is fairly satisfactory and could not be expected to be better, considering that the various data belong to different investigators and do not lend themselves to easy comparison.

In conclusion, let us point to another fact in favour of the above mechanism of detonation. On the basis of the diagram representing the normal velocities of flame propagation for air mixtures of various gases and vapour ([19]), we are able to predict in which particular case spark ignition is most likely to produce detonation. If we arrange the gases according to a decreasing aptitude to detonate, the next gas to follow after hydrogen and acetylene is ethylene, owing to its considerable velocity of flame propagation.

M. Rivin of our Institute has told us that he was able to observe detonation due to spark ignition in an air mixture of 6.5% ethylene contained in a 17 mm wide tube when the initial pressure was 4 atm. Further calculation shows that when the detonation sets in, the value of Re calculated as above passes through the critical value. No exact data being available on the variation of the normal velocity of flame propagation with the pressure, the calculation is only an approximate one and will not be given here.

The hypothesis presented here is thus seen to be supported by experimental evidence; it allows us at the same time to determine (on the basis of the data for the normal velocity) the limiting concentration and the minimum pressure at which spark ignition will initiate detonation in tubes.

It must be noted that the expression

$$P = Re_{cr} \frac{760\eta}{v r \delta_0} \text{ mm Hg}$$

can be used for the determination of the minimum pressure only if the velocity of propagation is independent of the pressure. Otherwise the dependence on pressure must be accounted for.

We wish to emphasize once more that all the above considerations refer to ignition by means of a weak agent (spark, flame). When the ignition is due to an extraneous detonation wave, the detonation starts at once, without preliminary acceleration of the flame, and the limiting concentrations in this case are determined by quite other factors.

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CHIMIE

LES NOUVEAUX PÉTROLES DU BASSIN DU VOLGA

(Nouveaux graphiques pour les pétroles)

Par W. W. TSCHELINZEFF, membre correspondant de l'Académie

I. LE PÉTROLE DE SYZRANE, SA CARACTÉRISTIQUE ET SON FENDAGE OXYDANT EN PHASE DE VAPEUR

Les couches des pétroles nouvellement découvertes au bassin du Volga et avant tout à Syzrane, ouvrent de nouvelles perspectives pour l'économie et l'industrie de ce bassin et de toute l'U. R. S. S.

Si l'on trace une ligne droite à partir de la région pétrolifère «Tchoussovski Gorodki» sur le fleuve Kama en traversant Ichimbaevo jusqu'au fleuve Emba et si on la prend ensuite pour base d'un triangle isocèle au sommet, relevé de 8° de longitude (de 56° à 48°), ce dernier tombe justement sur les nouvelles couches de Syzrane.

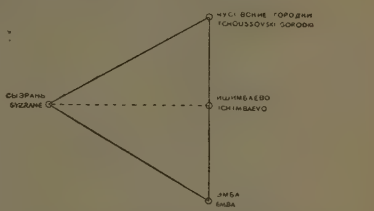

Fig. 1. La base du triangle 12° de latitude septentrionale (de 47° à 59°). Les angles à la base sont de 42° approximativement. La perpendiculaire est de 8° de longitude orientale (de 48° à 56°).

Notre expédition, organisée au mois de juin 1938, a pris un échantillon de pétrole du puits No. 17, dont le débit quotidien est de 70 tonnes de pétrole. Ce pétrole est relevé de la profondeur de 1100—1140 m de l'horizon «B», appartenant à l'étage Toornay du Carbone Inférieur C_1. Le gisement pétrolifère est situé à 8 km à peu près du Volga. Le pétrole puisé était suffisamment mobile.

Fractionnement. Soumis à la distillation d'après Engler, le pétrole donne les fractions suivantes. Point d'ébullition 76°; de 76 à 100°—2.0%; jusqu'à 110°—3.0%; jusqu'à 120°—4.0%; jusqu'à 130°—5.5%; jusqu'à 140°—7.0%; jusqu'à 150°—8.5%; jusqu'à 160°—10.5%; jusqu'à 170°—12.6%; jusqu'à 180°—14.5%; jusqu'à 190°—16.5%; jusqu'à 200° —18.5%. Ainsi le pétrole donne 18.5% de distillé de benzine.

Quant au distillé de kérosène, le pétrole donne dans l'intervalle de 200 à 300° les fractions suivantes: de 200 à 210°—1.0%; jusqu'à 220°—2.0%; jusqu'à 230°—3.5%; jusqu'à 240°—6.0%; jusqu'à 250°—8.0%; jusqu'à 260°—9.5%; jusqu'à 270°—11.0%; jusqu'à 280°—14.5%; jusqu'à 290°—17.0%; jusqu'à 300°—19.2%. De sorte que le pétrole a produit en tout 19.2% de distillé de kérosène. De 300° jusqu'à la fin de l'ébullition il a été obtenu 46.4% d'huile lourde. Les résidus constituent à peu près 16%.

Humidité. La détermination de l'humidité d'après Dine-Stark a démontré que le pétrole ne contient point d'eau.

Additions mécaniques. Il n'en a été trouvé que 0.002%.

Constantes physiques. Le poids spécifique $d_{20}^{0}/_{4}^{0}$=0.832—0.838; en moyenne—0.835. La viscosité d'après Engler: E_{10}=10.5; E_{20}=5.1; E_{50}=2.0. Point d'inflammabilité d'après Abel-Pensky est+10°.

Contenu des asphaltènes et des résines: les asphaltènes —4.48%, les résines d'accise—36.0%.

En comparant ces données à celles pour d'autres pétroles, on peut voir que celui de Syzrane possède des particularités le distinguant des pétroles orientaux, ses voisins—ceux de Tchoussovaia, d'Ichimbaevo et d'Emba, ainsi que de ceux du Caucase et d'Oukhta.

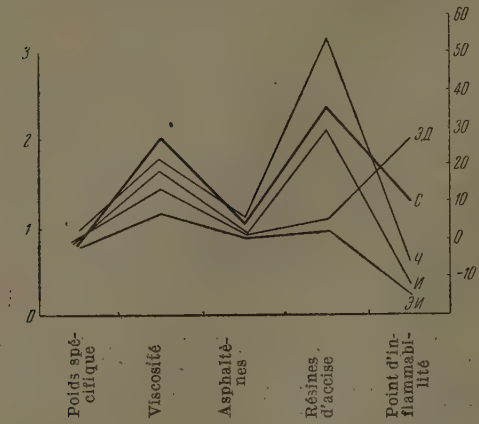

Fig. 2.

Pour bien démontrer les particularités du pétrole de Syzrane, nous avons composé des diagrammes spéciaux, où nous marquons sur les axes des coordonnées le poids spécifique et la viscosité (sur une échelle montrée du côté gauche du diagramme), ensuite le contenu en asphaltènes et en résines d'accise, ainsi que la température d'inflammabilité (sur une échelle donnée du côté droit du diagramme) (fig. 2).

On peut y voir que les 8 pétroles comparés se disposent par rapport à chacune des constantes étudiées dans l'ordre suivant.

Pour le poids spécifique: la première place est au pétrole Emba II—0.783; ensuite viennent celui de Grozny (faiblement paraffineux)—0.835, celui de Syzrane—0.835, le pétrole Emba I—0.864, celui d'Ichimbaevo—0.867, de Sourakhan NKP—0.873, de Stavropole—0.887, de Tchoussovaia—0.950.

Pour la viscosité (50°) la première place revient au pétrole de Grozny—1.05; suivent: l'Emba II—1.16, l'Emba I—1.44, celui de Sourakhan NKP—1.58, d'Ichimbaevo—1.65, de Tchoussovaia—1.74, de Stavropole—1.76, de Syzrane—2.0.

Pour le contenu des asphaltènes: la première place est occupée par pétrole Emba II—0; ensuite vient l'Emba I—des traces, le pétrole de Sourakhan NKP—des traces, celui d'Ichimbaevo—0.56, le pétrole faiblement paraffineux de Grozny—1.2, celui de Syzrane—4.48, de Stavropole—4.65, de Tchoussovaia—5.2.

Pour le contenu des résines d'accise: la première place est retenue par l'Emba II—2.0%; suivent: l'Emba I—5.0, le pétrole de Sourakhan NKP—8.6, le pétrole légèrement paraffineux de Grozny—16.0, d'Ichimbaevo—30.0, de Stavropole—34.0, de Syzrane—36.0, de Tchoussovaia—54.5.

Pour l'inflammabilité le pétrole Emba II se trouve à la première place—> —15°, ensuite viennent: celui d'Ichimbaevo—12°, de Grozny (faiblement paraffineux) — —11°, de Tchoussovaia — —7°, de Syzrane — +10°, de Stavropole— +10°, de Sourakhan NKP— +16°, l'Emba I— +27°.

Il suit de cette comparaison du pétrole de Syzrane à d'autres pétroles de l'U. R. S. S. que ses constantes caractéristiques lui assurent une place particulière; selon quelques-unes d'entre elles, il se trouve placé entre les pétroles d'Ichimbaevo et de Tchoussovaia, selon d'autres—il les dépasse.

Répartition des hydrocarbures de la benzine de Syzrane en groupes. Selon le caractère de ses parties inté-

grantes, la benzine de Syzrane se compose d'hydrocarbures, appartenant aux groupes suivants:

Hydrocarbures aromatiques	Hydrocarb. de la série du méthane	Hydrocarbures alycycliques	Hydrocarbures non-saturées
2.5%	76.6%	20.5%	0.4%

Les rendements en benzine et en kérosène du pétrole de Syzrane, ainsi que la répartition de sa benzine en groupes, peuvent être comparés à ceux d'autres pétroles soviétiques au moyen d'un diagramme spécial (fig. 3).

Les données y sont montrées sur la même échelle, qui nous a servi antérieurement à comparer le contenu des pétroles en asphaltènes et en résines d'accise. Pour tracer ce diagramme, nous avons assigné des places sur l'axe des abscisses aux rendements de benzine et de kérosène, ainsi qu'aux différents groupes des hydrocarbures, tout en marquant sur l'axe des ordonnées les chiffres y correspondants.

D'après ces données les différents pétroles comparés se rangent dans l'ordre suivant.

D'après les rendements de benzine vient en premier lieu l'Emba II, Iskiné et Saguize—39.6; suivent: le pétrole de Grozny—27.5, d'Ichimbaevo—27, de Tchoussovaia—24.5, de Syzrane—18.5, de Sourakhan—16.5, d'Emba I, Dossor, Costchaguil—11.0%.

Pour les rendements de kérosène, la première place appartient au pétrole de Sourakhan—32.8; ensuite viennent ceux d'Emba I, Dossor, Costchaguil—31.0, de Grozny—27.0, d'Emba II, Iskiné, Saguize—24.0, de Syzrane—19.2, d'Ichimbaevo—17.0, de Tchoussovaia—12.0%.

Pour le contenu des hydrocarbures aromatiques dans la benzine la première place est occupée par le pétrole de Tchoussovaia—48.0, suivi de celui d'Ichimbaevo—18.0, de Grozny—16.0, d'Emba II, Iskiné et Saguize—8.0, d'Emba I, Dossor et Costchaguil—4.0, de Sourakhan—2.6, de Syzrane—2.5%.

Pour le contenu de la benzine en alycarbures de la série du méthane, c'est le pétrole de Syzrane—76.6—qui prime, viennent ensuite ceux d'Emba II, Iskiné et Saguize—60.0, d'Ichimbaevo—56.0, de Grozny—52.0, de Sourakhan—35.5, d'Emba I, Dossor et Costchaguil—33.0, de Tchoussovaia—26.0%.

Pour le contenu de le benzine en alycycles la première place est tenue par le pétrole d'Emba I, Dossor et Costchaguil—63.0; suivent: celui de Sourakhan—61.9, de Grozny—33.0, d'Emba II, Iskiné et Saguize—32.0, d'Ichimbaevo—26.0, de Tchoussovaia—26.0, de Syzrane—20.5%.

Quant au contenu des benzines en hydrocarbures non-saturées, celle de Syzrane en contient 0.5%, les autres—0%.

Il suit des données, qui viennent d'être citées, que d'après ses rendements en benzine et en kérosène le pétrole de Syzrane occupe une place moyenne; d'après le contenu de sa benzine en hydrocarbures aromatiques et alycycliques—la dernière, et d'après le contenu de la benzine en hydrocarbures de la série du méthane—tour au contraire la première, et c'est ce qui le distingue surtout de tous les autres pétroles soviétiques.

Répartition des hydrocarbures du kérosène de Syzrane en groupes. Selon le caractère de ses parties intégrantes le kérosène de Syzrane se compose de groupes suivants d'hydrocarbures:

Hydrocarbures aromatiques	Hydrocarb. de la série du méthane	Hydrocarbures alycycliques	Hydrocarbures non-saturées
21.5%	16.2%	59.3%	2.6%

A l'encontre de la benzine, les alycycles y prévalent; puis viennent les hydrocarbures aromatiques, tandis que le contenu des hydrocarbures de la série du méthane tombe à un niveau fort bas.

Quantité du soufre dans le pétrole, la benzine et le kérosène de Syzrane. La quantité totale du soufre dans le pétrole de Syzrane s'est trouvée de 2.16%. En comparaison aux autres pétroles orientaux ce chiffre semble assez considérable. Le pétrole de Tchoussovaia—5.40%, d'Ichimbaevo—2.68%, de Syzrane—2.16%, d'Emba I—0. 11%.

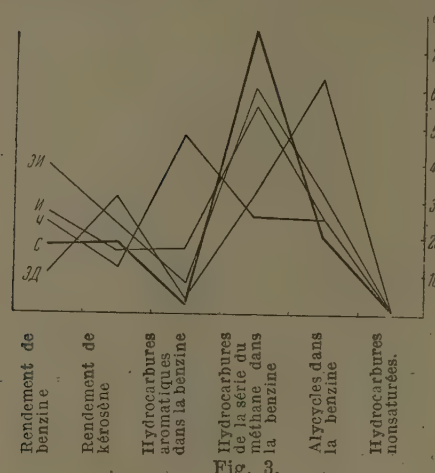

Fig. 3.

Lors de la distillation, les combinaisons sulfuriques du pétrole de Syzrane se distribuent entre la benzine et le kérosène de la manière suivante: la benzine de Syzrane (76—200°)—quantité totale de S=0.25%; le kérosène de Syzrane (200—300°)—quantité totale de S=0.98%.

Dans le but de comparaison nous citons aussi le contenu du soufre dans la benzine et le kérosène de distallation directe des pétroles de Tchoussovaia et d'Ichimbaevo.

Le pétrole de Tchoussovaia	Le pétrole d'Ichimbaevo
La benzine jusqu'à 160°: S=0.08	La benzine: S=0.72
Le pétrole 150—275°: S=1.42	Le kérosène: S=1.10

Le contenu considérable du soufre dans la benzine et le kérosène de Syzrane rend leur désulfuration nécessaire. La méthode la plus efficace d'élaboration et de désulfuration simultanées du pétrole de Syzrane est le fendage oxydant en phase de vapeur.

Fendage oxydant du pétrole de Syzrane en phase de vapeur. Ayant tiré du pétrole de Syzrane 18.5% de benzine contenant 0.25% de soufre, ainsi que 19.2% de kérosène contenant 0.98% de soufre, nous soumîmes le dernier au fendage oxydant en phase de vapeur. Ce processus répété une fois dans les conditions suivantes—550° de température, 200 l d'air pour 1 kg de kérosène, la vitesse du passage du produit de 100 g par heure pour 4 cm² de section—nous donna pour chaque kg de matière brute les quantités suivantes de produits liquides et gazeux: quantité totale de produits liquides—80.0%; les gaz (à l'exception du nitrogène de l'air)—70 l.

Les produits liquides sont distribués entre les fractions de la benzine (30—200°) et du kérosène (200—300°) comme suit: la benzine—35.0%; le kérosène—55.1%; les résidus—9.9%.

Le soufre s'y trouva réparti de la manière suivante: la benzine de fendage (550°)—quantité totale S=0.42%; le kérosène de fendage (550°)—quantité totale S=0.98%.

Donc, la quantité totale du soufre dans la benzine de fendage, comparée à celle du kérosène de distillation directe servant de matière première, s'est abaissée de 50%, tandis que la quantité du soufre dans le kérosène est restée la même.

Une seconde série d'expériences du fendage fut effectuée à la température de 600°, avec la même vitesse du passage du produit et la même quantité d'air—200 l pour chaque kg de kérosène. Répété une fois, le processus nous a donné: quantité totale de produits liquides—72.0%; les gaz (à l'exception du nitrogène de l'air)—200 l.

Les produits liquides sont distribués entre les fractions de la benzine (30—200°) et du kérosène (200—300°) de telle manière: la benzine—43.0%; le kérosène—48.6%; les résidus—8.4%.

Le soufre se trouve cette fois réparti ainsi: la benzine de fendage (600°)—quantité totale S=0.36%; le kérosène de fendage (600°)—quantité totale S=0.94%.

De sorte qu'à la suite de fendage oxydant en phase de vapeur mené à la température de 600° la quantité du soufre dans la benzine, comparée à celle du kérosène de distillation directe servant de matière première, se trouve réduite presqu'à 37% de la quantité primitive, tandis que dans le kérosène la quantité du soufre ne change que très peu. L'épuration ultérieure des benzines de fendage à l'aide de $ZnCl_2$ réduit le contenu en soufre à 0.1% et à 0.06%, autrement dit, en pratique la benzine se trouve désulfurée.

Les gaz, que l'on obtient à la suite de fendage oxydant en phase de vapeur, contiennent jusqu'à 60% et au délà de hydrocarbures non-saturées, ce qui les rend très importants comme matière première pour les synthèses organiques.

Ont pris part au travail: T. L. Dmitrieva, V. A. Polonnikova et A. S. Troubnikova.

II. LE PÉTROLE DE STAVROPOLE, SA CARACTÉRISTIQUE ET SON FENDAGE OXYDANT EN PHASE DE VAPEUR

Le second gisement pétrolifère dans le bassin du Volga, découvert en 1936, est situé au pied des monts Gigoulis, sur la rive droite du Volga, juste en face de Stavropole. La situation est parfaitement symétrique par rapport au gisement de Syzrane qui est placé vis-a-vis de l'autre côté du Bec de Samara, une distance de 0.3 km le sépare du fleuve Volga et 80 km environ de la ville Syzrane (fig. 1).

Fig. 1.

Notre expédition a pris au mois de juin 1938 un échantillon de pétrole du puits No. 1, d'où avait antérieurement jailli une fontaine de pétrole, donnant jusqu'à 300 tonnes toutes les 24 heures. Ici le pétrole est relevé de la profondeur de 991 m, de la couche «B», de dessous les calcaires de la Période Carbonifère.

Fractionnement. Soumis à la distillation d'après Engler le pétrole a donné les fractions suivantes. Le point d'ébullition 76°; de 76 à 100°—2%; jusqu'à 110°—3.6%; jusqu'à 120°—4.0%; jusqu'à 130°—4.5%; jusqu'à 140°—6%; jusqu'à 150°—8%; jusqu'à 160°—9%; jusqu'à 170°—10.5%; jusqu'à 180°—13%; jusqu'à 190°—15.5%; jusqu'à 200°—17.5%.

La distillation dans l'intervalle de 200 à 300° a fourni les fractions suivantes: de 200 à 210°—2%; jusqu'à 220°—3%; jusqu'à 230°—4%; jusqu'à 240°—5.5%; jusqu'à 250°—8.5%; jusqu'à 260°—11%; jusqu'à 270°—13%; jusqu'à 280°—16%; jusqu'à 290°—19%; jusqu'à 300°—22%.

De sorte qu'il a été obtenu: 17.5% de distillé de benzine, 22.0% de distillé de kérosène, 60.5% de résidu—produits lourds, donnant à la distillation 46.0% d'huile lourde. Le résidu après cracking—14.5%.

Humidité. La détermination de l'humidité d'après Dine-Stark a démontré que le pétrole ne contient point d'eau.

Additions mécaniques. Il n'en a été trouvé que 0.003% à peu près.

Constantes physiques. Le poids spécifique $d_{20/4}=0.887$. La viscosité d'aprés Engler: $E_{10}=77$; $E_{20}=4.1$; $E_{50}=1.7$. Le point d'inflammabilité d'après Abel-Pensky est $+10°$.

Contenu des asphaltènes et des résines d'accise: les asphaltènes—4.65%, les résines d'accise—34.0%.

Ces données nous montrent que malgré l'éloignement de 80 km du gisement de Syzrane, le pétrole de Stavropole par ses constantes principales est fort proche de celui de Syzrane. On peut dire, que ces deux pétroles semblent provenir du même réservoir naturel.

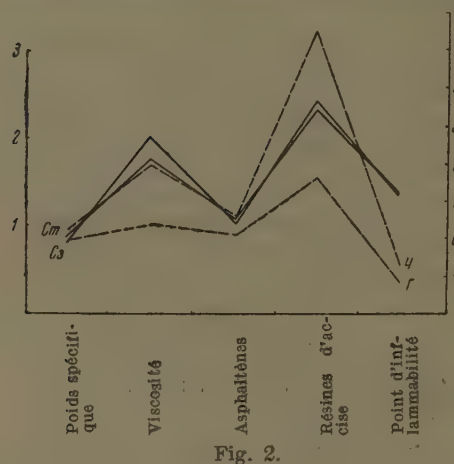

Fig. 2.

Pour bien démontrer la proche parenté des pétroles de Stavropole et de Syzrane, nous donnons un diagramme spécial, où nous marquons sur l'axe des ordonnées le poids spécifique et la viscosité (sur une échelle montrée du côté gauche du diagramme), ensuite le contenu en asphaltènes et en résines d'accise, ainsi que le point d'inflammabilité (sur une échelle placée du côté droit du diagramme).

En but de comparaison à d'autres pétroles de l'U. R. S. S. nous montrons aussi dans ce diagramme les données concernant le pétrole de Tchoussovaia et le pétrole faiblement paraffineux de Grozny, parce que ce sont ceux qui diffèrent le plus des pétroles du bassin du Volga. Ces dernières données sont marquées en pointillé (fig. 2).

Nous ne citons pas ici les autres pétroles soviétiques, mais les diagrammes de l'article sur le pétrole de Syzrane démontrent suffisamment de combien celui-là diffère des autres pétroles orientaux, ainsi que de ceux du Caucase et du Nord, par ses constantes principales.

On trouve dans les diagrammes mentionnés toutes les constantes déterminées pour les différents pétroles de l'U. R. S. S., ce qui permet de voir la place occupée par le pétrole de Stavropole parmi les autres.

Répartition des hydrocarbures de la benzine de Stavropole en groupes. Les hydrocarbures, composant la benzine de Stavropole, se subdivisent en groupes suivants:

Hydrocarbures aromatiques	Hydrocarb. de la série du méthane	Hydrocarbures alycycliques	Hydrocarbures non-saturées
1.9%	63.4%	34.3%	0.4%

Nous montrons dans un diagramme spécial les rendements en benzine et en kérosène du pétrole de Stavropole, ainsi que la répartition de sa benzine en groupes. Les données y sont fixées sur la même échelle, dont nous nous sommes servis dans le diagramme précédent pour marquer le contenu en asphaltènes et en résines d'accise.

Nous marquons sur l'axe des ordonnées de ce diagramme les rendements en benzine et en kérosène, ainsi que la répartition par groupes des hydrocarbures des benzines de Stavropole et de Syzrane et—comme comparaison—

les mêmes données pour les deux pétroles, dont ils diffèrent le plus, ceux de Grozny et de Tchoussovaia.

Quant aux autres pétroles, nous ne citons pas ici les données les concernant, mais les diagrammes, joints à l'article sur le pétrole de Syzrane, ainsi que les tableaux, qu'on y trouve, permettent de juger combien les pétroles du bassin du Volga diffèrent de ceux de l'Orient, du Caucase et du Nord.

En comparant le caractère du pétrole de Stavropole et de sa benzine à ceux du pétrole et de la benzine de Syzrane, nous ne découvrons pas de différence profonde. Leurs rendements en benzine (17.5% et 18.5%) et en kérosène (22% et 19.2%) sont presque égaux; tous les deux ne contiennent presque pas d'hydrocarbures aromatiques (1.9% et 2.5%), mais d'autant plus de ceux de la série du méthane (63.4% et 76.6%), une quantité moyenne d'alycycles (34.3% et 20.5%) et une quantité minimum d'hydrocarbures non-saturées (0.6% et 0.5%).

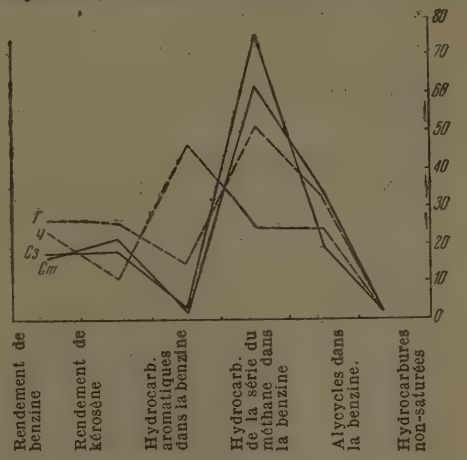

Fig. 3.

Si l'on peut nommer le pétrole de Tchoussovaia, vu la hauteur du contenu des hydrocarbures aromatiques dans ses benzines, un pétrole très aromatisé, si l'on peut caractériser les pétroles de Sourakhan NKP, de Dossor et de Costchaguil sur l'Emba comme des pétroles alycycliques, on doit classer le pétrole de Stavropole, et d'autant plus, celui de Syzrane, comme des pétroles hautement méthanés (fig. 3).

Répartition des hydrocarbures du kérosène de Stavropole par groupes. Selon le caractère des hydrocarbures composant le kérosène de Stavropole, ils se répartissent en groupes:

Hydrocarbures aromatiques	Hydrocarb. de la série du méthane	Hydrocarbures alycycliques	Hydrocarbures non-saturées
23.5%	81.1%	54.4%	3.0%

Comme on le voit, dans le kérosène de Stavropole, ainsi que dans celui de Syzrane, à l'encontre de leurs benzines, ce sont les alycycles qui prévalent, tandis que la quantité des hydrocarbures de la série du méthane s'abaisse de beaucoup.

Quantité de soufre dans le pétrole, la benzine et le kérosène. La quantité totale du soufre dans le pétrole de Stavropole se trouva de 2.10%, c'est-à-dire presque égale à celle du pétrole de Syzrane et de beaucoup plus petite que celle du pétrole d'Ichimbaevo. Le pétrole d'Ichimbaevo—2.68%; de Syzrane—2.16%; de Stavropole—2.10%; d'Emba I—0.11%.

Au cours de la distillation les combinaisons sulfuriques du pétrole de Stavropole se répartissent entre la benzine et le kérosène de la manière suivante: la benzine de Stavropole (76—200°)—quantité totale de S=0.17%; le kérosène de Stavropole (200—300°)—quantité totale de S=0.96%.

Dans le but de comparaison nous citons aussi le contenu du soufre dans la benzine et le kérosène de distillation directe d'autres pétroles:

Le pétrole de Tchoussovaia	Le pétrole d'Ichimbaevo
La benzine jusqu'à 160° : S=0.80%	La benzine : S=0.72%
Le kérosène 150—275° : S=1.42%	Le kérosène : S=1.10%

Le contenu considérable de soufre dans la benzine et le kérosène de Stavropole rend leur désulfuration nécessaire. Pour le pétrole de Stavropole, ainsi que pour celui de Syzrane on peut recommander le fendage oxydant en phase de vapeur comme la méthode la plus efficace d'élaboration et de désulfuration simultanées.

Fendage oxydant du pétrole de Stavropole en phase de vapeur. Ayant tiré du pétrole de Stavropole 17.5% de benzine contenant 0.17% de soufre, ainsi que 22.0% de kérosène contenant 0.96% de soufre, nous soumîmes le dernier au fendage oxydant en phase de vapeur.

Ce processus répété une fois dans les conditions suivantes—500° de température, 160 l d'air pour un kg de kérosène, la vitesse du passage du produit de 100 g par heure pour 4 cm^2 de section—nous donna pour chaque kg de matière première les quantités suivantes de produits liquides et de gaz: quantité totale de produits liquides—73%, les gaz (à l'exception du nitrogène de l'air)—64 l.

Les produits liquides se distribuent entre les fractions de benzine (30—200°) et celles du pétrole (200—300°) de la manière suivante; la benzine—17.5%; le kérosène—63.7%; le résidu—18.8%.

A la suite du fendage le soufre se trouva réparti de la manière suivante: la benzine de fendage (500°)—quantité totale S=0.52%; le kérosène de fendage (500°)—quantité totale S=0.90%.

Donc, la quantité totale du soufre dans la benzine comparée à celle du kérosène de distillation directe, servant de matière première, s'est considérablement abaissée, tandis que la quantité du soufre du pétrole est restée presque invariable.

Une seconde série d'expériences du fendage fut effectuée à la température de 550°, avec la même vitesse du passage du produit et la même quantité d'air—160 l pour chaque kg de pétrole. Répété une fois le processus nous a donné: quantité totale de produits liquides—74.4%; les gaz (à l'exception du nitrogène de l'air)—76 l.

Les produits liquides se répartirent entre les fractions de la benzine (30—200°) et du kérosène (200—300°) comme il suit: la benzine—27.0%; le kérosène—56.4%; le résidu—15.6%.

Le soufre se trouva cette fois réparti ainsi: la benzine de fendage (550°)—quantité totale S=0.42%; le kérosène de fendage (550°)—quantité totale S=0.90%.

Comme on voit, la quantité totale du soufre dans la benzine, comparée à celle du kérosène, servant de matière première, s'est abaissée à la suite du fendage oxydant en phase de vapeur mené à la température de 550° de plus de 50%, tandis que dans le kérosène elle ne diminue que fort peu. L'épuration ultérieure de la benzine à l'aide de $ZnCl_2$ réduit le contenu en soufre à 0.1—0.06%.

Les gaz, que l'on obtient à la suite du fendage oxydant du pétrole de Stavropole, sont de grande importance pour les synthèses organiques.

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CHEMISTRY

ON THE MECHANISM OF THE CORROSION OF COPPER IN ELECTROLYTES

By N. D. TOMASHOV

(Communicated by Wl. A. Kistiakowsky, Member of the Academy, 3. IV. 1939)

According to current opinions as to the nature of the solution of noble metals, for instance copper, mercury, silver etc., in acids and neutral electrolytes, it is considered that the initial stage of solution of these metals is the preliminary oxidation of the metal by oxygen of the air or by the oxidizing action of the solution itself, with subsequent solution of the metal oxide in the given electrolyte, i. e., it is interpreted as a pure chemical process, not connected with the necessity of the transfer of electrons.

Such a point of view with respect to the solution of copper is upheld, for example, by Tammann (1), Izgaryshev (2), Bengough (3). The same opinion is developed in the fundamental handbooks dealing with the corrosion of metals(4, 5).

Though Evans (6) is pointing to the possibility of a pure electrochemical mechanism, yet in principle he also supports the opinion of the necessity of the initial oxidation of copper during its solution. Such an opinion concerning the nature of the solution of the noble metals is in a certain logical contradiction to the generally accepted electrochemical mechanism of solution for most of the metals.

A more detailed study of this question and a number of experiments which we carried out, show that the explanation of the mechanism of the solution of these metals by way of preliminary oxidation can hardly be correct, and that the usual electrochemical theory of corrosion, upon a more detailed treatment of the processes of cathodic depolarization, is in more complete agreement with the experimental data.

It was pointed out by W. A. Kistiakowsky that the possibility of a corrosive process during oxidation will be determined by the relation between the potential of the metal and the potential of the oxygen electrode(7).

The reaction of cathodic depolarization is, essentially, a process of assimilation of an electron, i. e., the process of the reduction of some oxidizing-depolarizing agent, and therefore it may be considered that the potential of the local cathodes is determined by the potential of the oxidizing-reducing systems at the cathode. Hence, on the basis of the fundamental postulate of the electrochemical theory of the solution of metals, one may conclude that the process of the electrochemical solution of a metal is possible if $V_A < V_{R-O}$, where V_A is the potential of the metal forming the anode and V_{R-O} is the oxidation-reduction potential established on the cathode.

It is therefore quite natural that, during the working of a local element, an accumulation of the products of the reduction of the given oxidizing agent will occur on the cathode, and this will result in a certain debasing of the potential of the cathode (polarization). Polarization of the cathode will be the smaller (and, consequently, the corrosion process the more intensive), the larger the percent of the oxidizing agent at the cathode and the larger the rate of mixing of the electrolyte at the local cathode. (It stands to reason that this statement is valid only for cases of corrosion with a cathode control. When an anode control takes place, the increase of the concentration of the oxidizer may, on the contrary, reduce the rate of corrosion, owing to the establishment of passive state).

As follows from such a conception, all depolarization reactions which may occur on the cathode of a local element in the process of the corrosion of a metal, fit into the following scheme:

1) Discharge of cations. For example, the discharge of hydrogen ions: $H^{\cdot} + \ominus \rightarrow H$, or of metal ions: $Ag^{\cdot} + \ominus \rightarrow Ag$, and others.

2) The formation of anions. For example, $^1/_2\ O_2 + 2\ominus \rightarrow O''$ $\xrightarrow{H_2O}$ $2OH'$ or $^1/_2\ Cl_2 + \ominus \rightarrow Cl'$, etc.

3) Decrease in valency of cations. For example, $Cu^{\cdot\cdot} + \ominus \rightarrow Cu^{\cdot}$ or $Fe^{\cdot\cdot\cdot} + \ominus \rightarrow Fe^{\cdot\cdot}$, and others.

4) Increase in valency of anions. For example, $S_2O_8'' + 2\ominus \rightarrow 2SO_4''$ or $MnO_4' + \ominus \rightarrow MnO_4''$, etc.

1. Study of the Solution of Copper in a Local Element. The experimental proof of the possibility of an electrochemical mechanism for the solution of copper is established on the basis of a study of a local element with a dissolving copper anode. A study of the couple Cu-Pt showed that for the working of such a couple the necessary condition is the presence of an oxidizing agent at the cathode of the couple (Pt).

In Table 1 experimental results are given for measurements of the current strength in the couple Cu | 3%NaCl | Pt upon the addition of H_2O_2 to the cathode compartment (Pt).

The working surfaces of the Pt and Cu electrodes were equal to $2 \times 2 = 4$ cm² in this and all the following experiments and were separated from one another by a distance of 2 cm. The cathodic and anodic compartments were separated by a semipermeable membrane made of baked clay. The copper electrodes were prepared from electrolytic copper.

Table 1

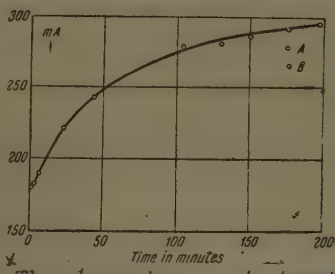
Current Strength in the Couple Cu | 3% NaCl | Pt upon the Addition of H_2O_2 to the Pt Compartment (10 min. after the addition of N_2O_2)

% H_2O_2	0.0	0.2	0.4	0.6
Current strength in mA	0.15	3.0	4.5	7.5

Experimental results show that the couple Cu|3%NaCl|Pt practically does not work, since, within a very short while after short-circuiting the couple, the Pt-cathode polarizes almost to the Cu-potential, and only a very insignificant current passes determined by the diffusion of oxygen to Pt. Addition of some oxidizing agent, for example H_2O_2 to Pt, markedly shifts the Pt-potential in the positive direction to such an extent that the poten-

tial which is being established on the Pt becomes considerably more positive than the potential of copper in the NaCl solution, as a result of which the solution of copper in the local element becomes possible. At the cathode (Pt) there occurs a process of assimilation of an electron by oxygen of the hydrogen peroxide (or directly by the hydrogen peroxide itself), i. e., the process $^1/_2\ O_2 + 2\ominus + H_2O \rightarrow 2OH'$ or directly $^1/_2\ H_2O_2 + \ominus \rightarrow OH'$.

The solution of copper in the couple $Cu|0.1N—(NH_4)_2SO_4|Pt$ will also occur upon the addition of ammonium persulfate to the cathodic compartment (to Pt). The results of this experiment are presented in Table 2. The working of this couple is determined by the concentration of persulfate at the cathode, since the current strength of the couple increases with an increase in the persulfate concentration at the Pt. An increase in persulfate at the anode (Cu) practically does not effect the current strength of the couple. Evidently in this case the following depolarization process (assimilation of electrons) occurs on the cathode: $S_2O_8'' + 2\ominus \rightarrow 2SO_4''$.



The change in current strength with time in the couple Cu |1N—$NaNO_3$| conc. HNO_3 |Pt. Point *A* denotes the value of the current strength which sets in upon stirring the nitric acid, point *B*, the current strength upon the addition of urea to nitric acid.

Similar results were obtained upon a study of the working of the couple Cu-Pt in nitric and sulfuric acids while alternately adding acid to the catholyte and the anolyte. In this case nitric or sulfuric acid is the depolarizing agent, nitrogen oxides being evolved at the cathode (Pt) when nitric acid is employed and sulfur dioxide being evolved when sulfuric acid is employed (when heated).

Table 2

Change in Current Strength in the Couple $Cu|0.1\ N—(NH_4)_2SO_4|Pt$ upon the Addition of $(NH_4)_2S_2O_8$ to the Pt-cathode and the Cu-anode (10 min. after the addition of persulfate)

Concentration of S_2O_8''									
	at the cathode (Pt)	0	0.001	0.01	0.1	1	0	0	0	0
	at the anode (Cu)	0	0	0	0	0	0.001	0.01	0.1	1
Current strength of the couple in mA		0.04	0.11	0.24	2.49	11.3	0.03	0.03	0.03	0.04

The current strength of the couple increases with the addition of the acid to the cathode and scarcely changes upon addition of the acid to the anode. The cathodic process of depolarization by nitric acid, evidently, can be represented by the following process: $H\cdot NO_3' + \ominus \rightarrow NO_2 + OH'$ or, which amounts to exactly the same thing, $NO_3' + \ominus \rightarrow NO_2 + O''$ and $O'' + H_2O \rightarrow 2OH'$. The cathodic polarization caused by sulfuric acid is evidently described by the process: $H_2SO_4 + 2\ominus \rightarrow SO_2 + 2OH'$.

It is known ([5]) that, during the solution of copper in nitric acid, acceleration of the process with time occurs. This is attributed to the formation of nitrous acid which exhibits a greater oxidizing action on copper. A decrease in the rate of solution of copper in nitric acid upon stirring the solution or upon the addition of urea is explained by the removal of nitrous acid from the copper surface.

The results of the study of the couple Cu |1N—$NaNO_3$| conc. HNO_3|Pt represented by the curve in the figure show, however, that:

1) The current strength of this couple considerably increases with time.

2) Stirring of the nitric acid solution or the addition of urea to the Pt-compartment noticeably decreases the current strength of the couple. On the curve represented in the figure, point *A* corresponds to the current strength which sets in upon stirring the nitric acid solution surrounding the Pt; and point *B*—to the current strength which sets in upon the addition of urea to the Pt-compartment until the nitric acid solution becomes decolorized.

It appears that all factors which change the rate of solution of copper in nitric acid show the same action on the working of the couple Cu-Pt as on the working of the couple, in which nitric acid is present only at the cathode (Pt).

From this it is logical to draw the conclusion that upon the solution of copper the oxidizing ability of the nitric acid and the nitrous acid forming immediately thereafter does not appear on the anodic dissolving parts of the copper, but on its cathodic parts, i. e., that the fundamental action of nitric acid on copper consists in depolarization of the cathodic parts.

On the whole, it can be stated with sufficient assurance that for the solution of copper it is not necessary for the oxidizing agent to have access to the dissolving surface of the metal, but only to the surfaces which act as local cathodes. Thus, the process of the solution of copper (and also other noble metals) in oxidizing agents should be conceived as a usual electrochemical process with oxidation-depolarization on local cathodes.

The explanation of the mechanism of the solution of metals occurring with the formation of complexes completely fits into the general scheme of the electrochemical solution of metals ([8], [9]).

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CHEMISTRY

OXIDATION OF COMPLEX COMPOUNDS OF BIVALENT PLATINUM WITH HYDROGEN PEROXIDE

By A. V. BABAJEVA

(Communicated by N. S. Kurnakov, Member of the Academy, 5. III.1939)

It is known that hydroxo-compounds of tetravalent platinum may easily be obtained by the oxidation of complexes of bivalent platinum with dilute hydrogen peroxide. This reaction was described by Chugajev and Khlopin (1), Greenberg and Filinow (2), and others.

Making use of their suggestions, we obtained the compound $[(NH_3)_2Pt(OH)_2Cl_2]$. In one experiment the hydrogen peroxide employed was not 10%, as is recommended by the mentioned writers, but stronger (about 20%). An analysis of the product obtained gave too small a value both for platinum and chlorine. This circumstance and, furthermore, the somewhat strange behaviour of the compound which was isolated, induced us to examine it in greater detail. The peculiarity of behaviour consisted in the fact that, upon standing for a long time in a weighing bottle placed in a desiccator at temperatures up to 45°C, the entire solid mass of the dry substance swelled owing to the gas evolved and changed in colour. Upon dissolving in water the dry freshly prepared substance, analysis of which gave consistent results, a vigorous evolution of gas was observed and the hydroxo-compound $[(NH_3)_2Pt(OH)_2Cl_2]$ which afterward could be crystallized out, remained in the solution.

It was natural to suppose that an intermediate compound was formed consisting of the complex molecule and hydrogen peroxide. A basis to this hypothesis can be found in the work of Černjaiev (3). This investigator studied the reaction of the nitration of cis-dinitropyridine and detected the formation of an intermediate compound $PtPy_2(NO_2)_2.HNO_3$ in the initial stage of the nitration, which is then oxidized to the nitronitrate $[PtPy_2(NO_2)_3NO_3]$.

Furthermore, the formation of an intermediate compound with hydrogen peroxide was assumed by Greenberg and Ptitzyn (4) in a paper which deals with the problem being considered here.

1. Peironnet salt $[(NH_3)_2PtCl_2]$ cis, while heating on a water bath, was treated with an excess of 30% hydrogen peroxide. At first the reaction goes on quietly, then, as heating proceeds, a vigorous evolution of gas begins, and the reaction soon stops. Plate-like crystals of a pale lemon colour are formed which in some experiments were separated from the mother liquid, while in others the solution was simply evaporated to drive off water and the excess of hydrogen peroxide. Analysis gave completely consistent results in both cases. After drying over sulphuric acid to constant weight, the salt was analyzed.

Found Pt — 53.13%, 53.11%, 53.32%. Cl_2 — 18.87%, 18.88%.

This analysis can correspond to one of two formulae: either to the hydroperoxide $[(NH_2)_3PtCl_2(OOH)_2]$, for which calculation gives Pt=53.31% and Cl_2=19.32% or to $(NH_3)_2\ PtCl_2.2H_2O_2$, for which calculation gives Pt=53.03% and Cl_2=19.25%.

In the second compound, the two hydrogen peroxide molecules either may be co-ordinated in the inner sphere or are located on the outside. In the latter case it should be possible to leach out these H_2O_2 molecules with ether. However, upon shaking the compound with absolute ether for several hours, we obtained negative results.

If one assumes that the hydroperoxide is formed, the H_2O_2 molecules either can in some way be held as a whole in the sphere of bivalent platinum $[(NH_3)_2PtCl_2.2H_2O_2]$, or oxidation of the platinum to the tetravalent form may take place and two electrons pass over to the two hydrogen peroxide molecules forming OOH′ ions which then are held by tetravalent platinum. The selection of one of the two possibilities could be made on the basis of a determination of the charge on the platinum. We titrated a solution of the compound obtained, made acid with sulphuric acid, with permanganate, remembering that both H_2O_2 and $Pt^{\cdot\cdot}$ should be titrated.

Results of the Titration

1. Calculated number of cm³ of $KMnO_4$ necessary for H_2O_2 and $Pt^{\cdot\cdot}$ — 23.3 cm³. Calculated number of cm³ of $KMnO_4$ necessary for H_2O_2 — 15.5 cm³. Number of cm³ of $KMnO_4$ found — 7.4 cm³.
2. Calculated number of cm³ of $KMnO_4$ necessary for H_2O_2 and $Pt^{\cdot\cdot}$—11.85 cm³. Calculated number of cm³ of $KMnO_4$ necessary for H_2O_2 — 7.25 cm³. Number of cm³ of $KMnO_4$ found — 4.1 cm³.

Consequently, in this case we are dealing with a compound of tetravalent platinum; the low results obtained in the titration of hydrogen peroxide are explained by the fact that, upon the action of water, this compound begins to evolve oxygen.

On the basis of these experiments we deem it possible to state that actually, upon the action of concentrated H_2O_2 on Peironnet salt, the hydroperoxide compound $[(NH_3)_2\ PtCl_2(OOH)_2]$ is formed, and the oxidation process may be represented by the following scheme:

$$[(NH_3)_2PtCl_2] + 3H_2O_2 \rightarrow [(NH_3)_2PtCl_2(OOH)_2] + 2H_2O.$$

Upon drying in an oven at 120°C, $[(NH_3)_2PtCl_2(OOH)_2]$ decomposes with the formation of a dihydroxo-compound according to the equation:

$$[(NH_3)_2PtCl_2(OOH)_2] = [(NH_3)_2PtCl_2(OH)_2] + O_2.$$

Upon treating $[(NH_3)_2PtCl_2(OOH)_2]$ two or three times with water on a water bath, it passes over into a dihydroxo-derivative with the evolution of oxygen.

Upon the action of hydrochloric acid both on $[(NH_3)_2PtCl_2(OOH)_2]$ and on $[(NH_3)_2PtCl_2(OH)_2]$, Cleve diamine $[(NH_3)_2PtCl_4]$ is always obtained.

Assuming that upon the action of an aqueous HCl solution a hydroxo-compound is obtained first, and that then OH′ is replaced by Cl′, we attempted to make dry HCl act on the hydroperoxo-compound, in the hope to obtain $[(NH_3)_2PtCl_2\ (OCl)_2]$ according to the equation:

$$[(NH_3)PtCl_2(OOH)_2] + HCl \rightarrow [(NH_3)_2PtCl_2(OCl)_2].$$

The dry hydroperoxide was kept in an atmosphere of dry HCl for 2—3 days. Usually, after the sample was subjected to the action of HCl, it pos-

sessed an odour of chlorine. In one of the experiments this reaction with dry HCl led to a product having the following composition: $[(NH_3)_2PtCl_2 \cdot OOH \cdot OCl]$. Analysis gave:

Found: Pt — 50.35%; Cl_2 — 27.76%.
Calculated: Pt — 50.76%; Cl_2 — 27.65%.

2. Upon oxidation of the second Reizet salt

$$\left[\begin{matrix} NH_3 & & Cl \\ & Pt & \\ Cl & & NH_3 \end{matrix}\right]$$

with 30% H_2O_2, large crystals separate out; they have the colour of egg yolk and dissolve in water with the evolution of oxygen. Evidently, the reaction proceeds here similar to the way it does in the case of a cis-diamine, i. e., Peironnet salt, viz., first a hydroperoxo-compound is formed:

$$\left[\begin{matrix} & OOH & \\ NH_3 & & Cl \\ & Pt & \\ Cl & & NH_3 \\ & OOH & \end{matrix}\right]$$

for which analysis gave:

Found: Pt — 53.58%, 53.17%; Cl_2 — 18.98%, 19.07%.
Calculated: Pt — 53.31%; Cl_2 — 19.32%.

Titration with $KMnO_4$ confirmed the assumption made regarding the structure of this compound.

Results of Titration

Calculated number of cm^3 of $KMnO_4$ necessary for H_2O_2 and $Pt^{\cdot\cdot}$ — 14.81 cm^3. Calculated number of cm^3 of $KMnO_4$ necessary for H_2O_2 — 9.21 cm^3. Number of cm^3 of $KMnO_4$ found — 5.4 cm^3.

Upon the action of water the hydroperoxide of the second Reizet salt passes over into the corresponding dihydroxo-derivative $[(NH_3)_2PtCl_2(OH)_2]$. For the latter, analysis gave:

Found: Pt — 58.21%; Cl_2 — 20.82%.
Calculated: Pt — 58.41%; Cl_2 — 21.22%.

3. The oxidation of cis-dinitrite $[(NH_3)_2Pt(NO_2)_2]$ with 30% H_2O_2 while heating the reactants on a water bath does not lead at once to a hydroperoxo-compound. Treatment with excess H_2O_2 some three or four times is necessary to obtain a homogeneous product.

The hydroperoxide

$$\left[\begin{matrix} & OOH & \\ NH_3 & & NO_2 \\ & Pt & \\ NO_2 & & NH_3 \\ & OOH & \end{matrix}\right]$$

appears as white crystals which are soluble in excess of hydrogen peroxide. Analysis gave:

Found: Pt — 50.15%, 50.49%; N_2 — 15.13%.
Calculated: Pt — 50.41%; N_2 — 14.46%.

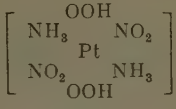
Similar to the case of chlorides, heating the hydroperoxide with water leads to transformation into the dihydroxo-compound $[(NH_3)Pt(NO_2)_2(OH)_2]$. This is accompanied by copious evolution of oxygen. Analysis gave:

Found: Pt — 54.88%.
Calculated: Pt — 54.95%.

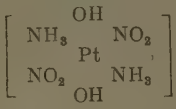
Upon treating either the hydroperoxide or the dihydroxo-compound with hydrochloric acid, Blomstrand salt is formed $[(NH_3)Pt(NO_2)_2Cl_2]$. Analysis gave:

Found: Pt — 49.40%.
Calculated: Pt — 49.78%.

4. When we attempted to obtain a hydroperoxide compound of the trans-dinitrite



we always obtained the dihydroxo-compound



in the form of beautiful white crystals. Analysis gave:

Found: Pt — 54.80%, 55.01%; N_2 — 15.89%.
Calculated: Pt — 54.95%; N_2 — 15.76%.

Evidently, the corresponding hydroperoxo-compound is not very stable and easily decomposes to form the dihydroxo-compound. However, about twice we succeeded in separating a compound containing 51.17% Pt. This was accomplished by very protracted evaporation of the trans-dinitrite with a large excess of hydrogen peroxide. Upon treating the compound obtained with water, oxygen was evolved and the dihydroxo-derivative was formed.

5. Cis-dipyridine dichloride, Py_2PtCl_2, upon oxidation with hydrogen peroxide, forms the dihydroxo-compound $Py_2PtCl_2(OH)_2$ directly. The latter dissolves very well in water and may be isolated in the form of small orange crystals by evaporating the solution. Analysis gave:

Found: Pt — 42.42%, 42.68%, 42.39%; Cl_2 — 15.70%.
Calculated: Pt — 42.60%; Cl_2 — 15.47%.

This compound cannot be titrated with $KMnO_4$ at all, and this is another proof of the absence of an OOH group in it.

6. The trans-compound Py_2PtCl_2 was not oxidized at all with hydrogen peroxide in spite of the fact that it was treated several times with a large excess of hydrogen peroxide while heating.

Analysis of the original simple Py_2PtCl_2 gave:

Pt — 46.02%; Cl_2 — 16.72%.

Analysis after treatment with hydrogen peroxide gave:

Pt — 45.61%, 46.34%; Cl_2 — 16.94%.

The hydroperoxo-compounds described in this communication may be obtained not only by oxidizing the non-electrolytes $[(NH_3)_2PtCl_2]$ cis and trans and $[(NH_3)Pt(NO_2)_2]$ cis with concentrated hydrogen peroxide, but also by interaction of the corresponding dihydroxo-compounds with excess of hydrogen peroxide (repeated evaporation on a water bath).

This process of the formation of hydroperoxides and dihydroxo-compounds should be regarded as a reversible process taking place according to the following scheme:

$$[(NH_3)_2Pt(OOH)_2X_2] + H_2O \rightarrow [(NH_3)_2Pt(OH)_2X_2] + O_2 + H_2O$$
$$[(NH_3)_2Pt(OH)_2X_2] + 2HOOH \rightarrow [(NH_3)_2Pt(OOH)_2X_2] + 2H_2O.$$

Conclusions: 1. The action of 30% hydrogen peroxide on Peironnet salt $\left[\begin{matrix} NH_3 & Cl \\ & Pt \\ NH_3 & Cl \end{matrix}\right]$, on the second Reizet salt $\left[\begin{matrix} NH_3 & Cl \\ & Pt \\ Cl & NH_3 \end{matrix}\right]$ and on cis-dinitrite $\left[\begin{matrix} NH_3 & NO_2 \\ & Pt \\ NH_3 & NO_2 \end{matrix}\right]$ leads to the formation of the corresponding hydroperoxides having the composition $[(NH_3)_2Pt(OOH)_2X_2]$.

2. The trans-dinitrite $\left[\begin{matrix} NH_3 & NO_2 \\ & Pt \\ NO_2 & NH_3 \end{matrix}\right]$ yields a very unstable hydroperoxo-compound which was not isolated.

3. Cis-pyridine chloride $[Py_2PtCl_2]$ is oxidized with hydrogen peroxide directly to $[Py_2PtCl_2(OH)_2]$. The trans-pyridine chloride is not oxidized at all.

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CHIMIE

SUR LES FORMULES ÉLECTRONIQUES DE LA DOUBLE ET TRIPLE LIAISON *

Par W. A. ISMAÏLSKI

(Présenté par E. Poraj-Kochitz, de l'Académie, le 10. IV. 1939)

Pour formuler la double et triple liaison d'après la théorie Lewis-Langmuir on emploie habituellement des schémas dont les doublets sont disposés horizontalement (I) ou verticalement (II):

I. :C̈::C̈: :C:::C: II. :C̈⋮C̈: :C⋮C:

Au point de vue de la théorie classique du tetraèdre l'idée de la distribution des électrons en forme de quatre doublets avec une formation de quatre paires de doublets autour de chaque atome ([12]) s'y efface; de plus dans les schémas II le caractère isolé des paires électroniques est de même effacé. Mais ces schémas sont encore moins satisfaisants au point de vue des idées modernes sur la double et triple liaison, créées par la théorie quantique**.

En même temps cette méthode de formuler remplit les formules des combinaisons plus compliquées d'une multitude de signes pointillés ([4]), dont elles sont bariolées au point de devenir très peu lisibles. Cet inconvénient est surtout très marqué dans les formules électroniques de la benzène (Lowry, Kermack, Robinson etc.)([5]).

Les formules électroniques deviennent beaucoup plus lisibles, si l'on emploie un procédé simplifié de formulation avec recours au trait de liaison («Strich»), servant de symbole de doublet ([6]). L'avantage des formules pareilles—par exemple III—consiste en leur ressemblance aux formules classiques structurelles habituelles:

III. H—N(H)—H IV. H[N̲]H V. H—N̲—H

Robinson Baumgarten Eistert

Nous sommes d'accord avec Eistert ([7]), que la méthode proposée par Baumgarten de représenter la liaison par un doublet par un trait transversal (IV),

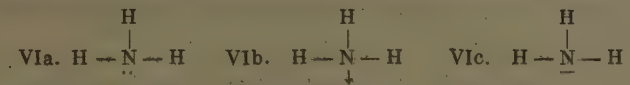
* Une communication sur la méthode de formulation décrite ci-dessus a été faite dans notre conférence «Le problème de liaison du groupe auxochrome» (présenté à la session sur les matières colorantes de la Section des Sciences Techniques de l'Académie des Sciences de l'URSS le 26 Février 1937) et aux sessions sur la sulfonation, les diazocombinaisons et la fusion alcaline, organisées par la Section des Sciences Techniques de l'Académie (1937—1938)([1]). Voir aussi W. A. Ismaïlski et Smirnov([2]).

** Voir sur les deux types des électrons du carbon du 1-r et 2-me genres: E. Hückel([17]), R. Truchet([3]), F. Hund ([18]).

visant à une plus grande vitesse d'expression graphique, est incommode et ne présente aucun avantage, en comparaison aux formules de Robinson.

L'emploi du symbole «trait de liaison» seulement ne permet pourtant pas de signaler dans la formule la différence entre le doublet liant deux atomes et le doublet libre (ou «actif»). Donc, Eistert propose l'emploi de deux signes: trait de liaison et trait transversal (V). Nous trouvons plus commode ([8]) d'employer pour le même but l'ancien symbole de Lewis, c'est-à-dire deux points (VIa) ([6]) ou bien une flèche (VIb), en élargissant l'application de ce symbole, proposé par Sidgwick ([9])*.

Si l'on prend le signe du trait transversal comme symbole du doublet actif, il nous paraîtrait utile, au point de vue graphique, de le présenter par un trait deux fois plus court que le trait d'union habituel (VIc):



VIa. $H-\underset{\cdot\cdot}{N}-H$ VIb. $H-\underset{\downarrow}{N}-H$ VIc. $H-\underline{N}-H$

Vu la nécessité de marquer quelquefois dans les formules la polarité de liaison et le rapprochement du doublet aux atomes isolés, ainsi que le rôle de la saturation de coordination dans les processus électromères, ayant en vue les conclusions de la théorie quantique, nous trouvons utile de soumettre à une discussion les règles de construction des formules électroniques, qui suivent.

1. Le squelette essentiel de la molécule, à savoir, toutes les liaisons principales [liaisons σ, réalisées par les electrons de la première espèce ([18],[17],[3])], est représenté à l'aide des signes de trait de liaison. La détalisation de la structure électronique n'est effectuée que dans une certaine partie de la molécule et au degré nécessaire.

2. Les formes diverses de la valence libre sont exprimées de la façon suivante:

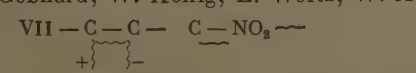
a) électrons isolés («libres») dans les radicaux—par un point (.)**.

b) doublets libres («actifs», «oniums»)—par leur signe usuel (:) (VIa) ou par une flèche ($\rightarrow$) (VIb), symbole de la «valence donnatrice».

c) lacunes électroniques («Lücken») (places privées de doublets) sont marquées par une absence de symbole, indiquant la présence des électrons.

3. La liaison ionisée est représentée par un trait transversal de longueur normale (en cas de nécessité accompagné par des signes $\pm$),+ $RNH_3|Cl^-$, Na|Cl, ou par une parenthèse dans les cas où l'on désire de souligner le caractère complexe du ion $RNH_3]^+$ Cl.

Le signe du trait ondulé (VII), proposé par Baeyer et admis dans une série de travaux ultérieurs (Gebhard, W. König, E. Weitz, W. A. Ismaïlski etc.)



VII $-C-C-\quad C-NO_2$ (ondulé)

nous semble utile pour la représentation de la valence ionogène et de la valence partielle ionisée dans des systèmes de résonance («charge distribuée»([11]), «liaisons par électrons fractionnés»).

4. Pour exprimer la polarité de la liaison dans une formule, il nous semble utile d'employer le symbole du «trait polaire», que l'on exprime par un trait interrompu par un doublet dans la place correspondante (ou ayant un doublet

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* Il n'est utile de conserver le signe de la flèche ($\rightarrow$) que pour l'expression de la liaison de coordination et du doublet actif. On peut en éviter l'emploi pour l'expression de la liaison polaire ([22]) en cas de l'emploi pour ce but du «trait polaire» («polarer Strich»).

** Le signe spécial de la petite croix ($\times$) au lieu du point pour exprimer les électrons de la seconde espèce, comme le propose E. Hückel, peut être utile dans des cas spéciaux.

à la fin) —: — ; —: (VIII), ou bien encore par un trait barré par une ligne courte —|—, —|— (IX) pour faciliter l'expression graphique de la formule.

VIII. C — : — C
C — : — C ou C — : C
C — : — Mg ou C : — Mg
C — : — O — : — H ou C — : O : — H

IX. C —|— C
C —|— C ou C —|— C
C —|— Mg ou C |— Mg
C —|— O —|— H, C —|— O |— H

X. C : C x
C : C Xa. C : C
C : Mg x
C : O : H

L'emploi des distances différentes entre le doublet et les atomes (X), que nous trouvons parfois dans certains travaux [10], ne donne point de schéma graphique assez distinct, surtout dans les molécules plus compliquées (noyau benzéniques).

5. Lors de la formulation de la liaison double et triple, vu la nature particulière de la seconde et de la troisième liaison [liaisons π [18] à l'aide des électrons de la seconde espèce [17,3]] qui fut démontrée par la théorie quantique, la liaison principale (σ) est représentée par un trait normale et la seconde et la troisième (π) le sont par des arcs $-\overset{\frown}{C-C}-$, $-\overset{\frown}{C-C}-$ *.

Pour ne pas être confondu avec l'arc de Thiele, servant de symbole de la liaison partielle $-C\overset{\frown}{=}C-$, l'arc, qui indique la liaison π, doit être placé plus haut et lier les sommets des lettres. L'emploi de l'arc dans les deux cas exprime en même temps la similarité des phénomènes, ces liaisons partielles pouvant apparaître au dépens des électrons de la seconde espèce et de l'affaiblissement de la liaison π.

En employant le trait polaire nous sommes aussi en état d'exprimer dans le schéma les idées de la polarité (XI, XII, XIII, XIV). En indiquant la polarité dans la seconde liaison, nous indiquons en même temps la présence des phénomènes analogues dans la liaison principale.

XI. $\overset{\frown}{C-C}$ $\overset{\frown}{C-C}$ $\overset{\frown}{C-O}$:

XII. $\overset{\frown}{C-C}$ $\overset{\frown}{C-C}$ $\overset{\frown}{C-C}$

XIII. $-\overset{\frown}{C-C}-$ $-\overset{\frown}{C-C}-$

XIV. $\overset{\frown}{C-N}$ $\overset{\frown}{C-N}$

Les formules électroniques, construites conformément aux règles décrites ci-dessus, ne sont pas surchargées de signes pointillés et sont assez bien lisibles.

Dans les formules des systèmes conjugués, contenant des hétéro-atomes (systèmes hétéro-énoïdes) [6], des auxo-atomes (systèmes auxo-énoïdes) [2], on réussit d'exprimer nettement l'influence, exercée sur l'état des systèmes conjugués des dérivés aromatiques par la tendance vers la saturation de coordination des auxo-atomes [2]. Nous nous proposons de faire une analyse plus détaillée de ce problème dans une communication spéciale; dans le Mémoire présent nous allons examiner le problème de la formulation électronique de la structure des molécules isostères.

Les formules électroniques des isostères doivent mettre en évidence la profonde ressemblance des couches extérieures des électrons entourant

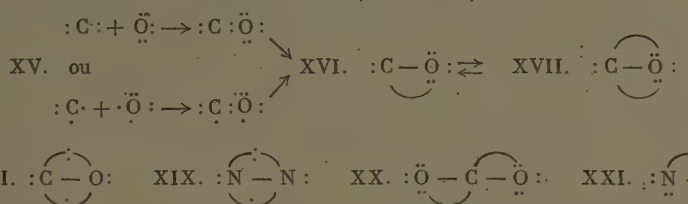
* Comp. notre désignation avec la proposition de E. Hückel de formuler la double liaison (σ, π) de la manière suivante : v. Xa.

les atomes séparés, ainsi que toute la molécule, et montrer la cause de l'apparition de ces structures.

Les formules électroniques structurelles acquièrent dans certains cas un fondement logique, si en les construisant l'on considère la tendance vers la saturation maximum des valences partielles* et de coordination: *en principe chaque molécule cherche à acquérir une saturation électronique, marquée par une saturation maximum des valences partielles et de coordination.* Les auxo-atomes non-saturés au point de vue de coordination, comme N, O, S avec des doublets actifs libres (doublets onium), cherchent à les saturer à l'aide des atomes voisins au moyen d'un processus électromère, ou dans une liaison double voisine, ou bien encore dans un système conjugué (énoïde).

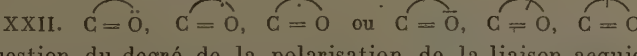
La formule électronique de l'oxyde de carbone C≡O proposée par Langmuir ([13]) était construite à base des mesures du moment dipolaire. Elle «ne fut pas acceptée par les chimistes organiciens» ([15]) parce que la structure donnée y est assez mal fondée au point de vue de la théorie de la valence du carbone.

Si l'on prend pour base la règle mentionnée, cette structure peut être établie de la façon suivante: un atome d'oxygène se lie à un atome C, avec une formation de XVI, après quoi une saturation du doublet actif de l'atome O se produit à l'aide d'une place privée de doublet dans l'atome C, avec une formation de la structure XVII (ou XVIII)**.



La génétique et la ressemblance des molécules isostériques CO et N_2, CO_2 et N_2O peuvent être exprimées par les schémas XVIII et XIX, XX et XXI.

En ce qui concerne le schéma C⇇O, où la flèche indique la direction de la liaison de coordination complémentaire, il faut noter, que cette flèche n'indique point le degré du déplacement du doublet que l'on peut représenter sous forme d'un des états du XXII, qui suivent (marqués par des moments dipolaires différents):



La question du degré de la polarisation de la liaison acquiert parfois une grande importance—lors de la discussion des propriétés du groupe azo et de son rôle dans les combinaisons azo, par exemple. La structure du groupe azo peut être représentée par les formes de résonance suivantes (XXIII***).

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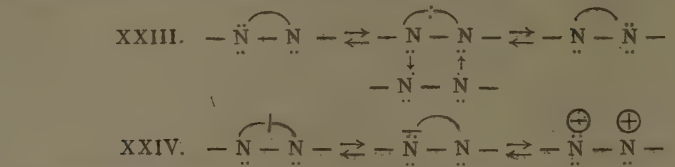
* Les «valences partielles» ont reçues un fondement physique dans la théorie quantique [E. Hückel ([17]), Arndt ([19]), Eistert ([19])—mésomérie, mésostructure; Pauling ([11]), Pestemer ([11])—résonance]. Les termes «mésoforme», «méso-état» (chromoétat([21]) lors de la discussion des problèmes de la coloration) ont été proposés par W. Ismaïlski([20]) encore en 1913—1915; leur contenu correspond à celui du «Zwischenzustand», de «l'état mésomère» (Arndt et Eistert, E. Hückel), «état de résonance» (Pauling).

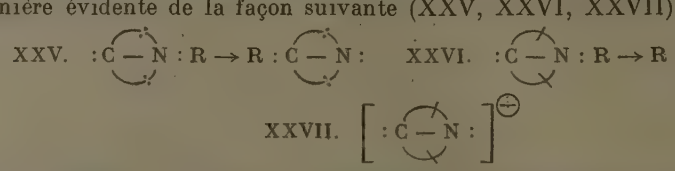
** Ces formules correspondent à deux formes de résonance de Pauling ([14]). Nous citons sa formule, pour qu'on puisse la comparer à la notre: :C: : O: ⇄ :C : : : O: Comp. Sidgwick ([15]).

*** Cet état, produit par des «influences contra» ([2]), provoque les propriétés chromophores du groupe azo.

En présence des influences polarisantes, on peut s'attendre à une transformation de la forme non-polarisée dans une forme polarisée, dont l'état terminal est la forme ionisée (XXIV).



La transformation de l'isonitrile en nitrile, la tautomérie de l'acide hydrocyanique, la structure des ions $(CN)'$ peuvent être formulées d'une manière évidente de la façon suivante (XXV, XXVI, XXVII).



Les formules de nitrile et isonitrile, citées ci-dessus, mettent en évidence les causes qui déterminent la structure du groupe (CN), la ressemblance structurelle entre le groupe nitrile et le groupe isonitrile, les causes qui produisent l'apparition chez les isonitriles des propriétés d'une combinaison avec un atome C «bivalent» (la présence d'une liaison triple et d'un doublet libre dans l'atome C, ainsi que dans l'oxyde de carbone) et que les formules des isonitriles avec un atome pentavalent ne sont pas valables.

Nous sommes d'avis que la méthode de construire des formules électroniques proposée a une certaine valeur au point de vue de l'enseignement.

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CHEMISTRY

CARBON DIOXIDE REDUCTION

By D. A. FRANK-KAMENETZKY

(Communicated by Wl. A. Kistiakowsky, Member of the Academy, 8. IV. 1939)

The kinetics of the reduction of carbon dioxide by activated ash-free sugar carbon has been measured under static conditions at temperatures ranging from 600 to 900° C and at pressures of the order of 50—200 mm Hg. The experimental method used was similar to that of Broom and Travers (1); the principal improvement related to the method of analysis. The course of the reaction was followed by measuring the heat conductivity of the gas mixture.

The principal results of the investigation are as follows. If the carbon surface is cleaned by evacuating to 10^{-3} mm Hg at 900° C, a measurable reaction takes place at any temperature above 600° C. In the temperature interval from 600 to 750°C the reaction proceeds according to the equation:

$$CO_2 + C = CO + [CO] \qquad (1)$$

where [CO] denotes a surface oxide of carbon which can be regarded as chemisorbed CO. Within the above temperature interval the total pressure, after an initial drop, remains approximately constant. At temperatures between 750 and 900°C the reaction is accompanied by a steady increase of pressure, which however in the initial stages is not equivalent to the amount of CO formed.

At temperatures from 400 to 600°C no transformation of CO into CO_2 has been observed. At these temperatures the interaction of CO_2 with carbon results only in a fall of the pressure during 2 to 5 min. The process appears to present a kind of activated adsorption of carbon dioxide by carbon:

$$CO_2 \rightarrow [CO_2]. \qquad (2)$$

It is obvious that the initial drop of pressure observed between 600 and 750°C is related to the same phenomenon which, at these temperatures, is superposed on reaction (1). The phenomena observed at 750—900°C can be regarded as a mutual superposition of process (1) and of [CO] desorption:

$$[CO] \rightarrow CO. \qquad (3)$$

In the course of the reaction itself and after the adsorption of CO the velocity of the reaction decreased. If after an experiment the carbon surface had not been cleaned at 900°C, the velocity of the reaction, at temperatures between 600 and 750°C, became considerably less than on a surface cleaned by the adopted method. At the initial stages the course of the reac-

tion with the time did not follow any simple law. Only at higher temperatures, especially in experiments with a small amount of carbon, the dependence of lg p_{CO_2} on the time became ultimately linear, corresponding to a first order reaction under stationary surface conditions.

The order of the reaction with respect to the initial CO_2 pressure was between zero and one, approaching zero at the lower temperature and higher pressures, and one—at the higher temperatures and lower pressures.

On a surface cleaned under conditions specified above the rate of the reaction was fairly consistent. This is in accord with observations reported by Garner (2), Broom and Travers (1) and others on the reproducibility of standard surface conditions after a similar treatment.

At least two forms of surface carbon oxides must play a part in the phenomena described: the one, denoted as $[CO_2]$, may be regarded as chemisorbed carbon dioxide; the other, [CO], as chemisorbed carbon monoxide. The last cannot act chemically or electrochemically as oxygen, since such a process would correspond to the liberation of free oxygen from CO which, under any actual conditions, is impossible from a thermodynamical point of view.

The quantitative results of the kinetic measurements will be published elsewhere. Here we shall discuss only the order of magnitude of the velocities of the various processes involved. At room temperature only the process of a physical CO_2-adsorption can be observed, and its velocity is immeasurably high. At temperatures between 600 and 750° C the activated CO_2-adsorption is accomplished within a time interval not exceeding 2—5 min. At these temperatures process (1) leads to a steady condition of the surface only after several hours. The adsorption of CO is a still slower process.

At low temperatures the activated CO_2-adsorption (2) may be regarded as an irreversible process. But at the temperatures at which reaction (1) proceeds, the CO_2-adsorption (2) is much more rapid than reaction (1) and, compared with the latter, can be regarded as a reversible process.

The following two schemes of the reaction mechanism can equally satisfactorily explain the phenomena observed. In the first place, reaction (1) may proceed by direct impact of activated CO_2-molecules on the carbon surface free from [CO] and $[CO_2]$. This conception seems to be supported by a fact observed by Langmuir (3) and confirmed by Eucken and Sihvonen (4) that in high-vacuum experiments the reaction requires preheating of the gas (and not only of the carbon filament). But even the latter fact may be explained on the basis of a second assumption, according to which the first step of the reaction consists in the activated CO_2-adsorption (2) followed by the reaction of chemisorbed $[CO_2]$ with a carbon surface free from [CO]. At room temperature the activated adsorption (2) has a negligibly small velocity, hence the necessity of pre-heating the gas. But at the temperatures at which reaction (1) proceeds, the activated adsorption (2) can be regarded as reversible in comparison with reaction (1), leading to the kinetic relationships observed.

It seems that the choice between the two schemes cannot be based on kinetic experiments conducted at ordinary pressures, since they both predict essentially the same kinetics. Only more detailed high-vacuum experiments using Langmuir's technique will lead to a definite conclusion.

The results of the present investigation may be of interest for the theory of the combustion of carbon.

According to our results, at temperatures near 600° C and in presence of CO_2, the carbon surface is completely covered with chemisorbed carbon oxides. But as a matter of fact, the reaction of carbon with oxygen proceeds at ordinary pressures at these and even lower temperatures, though the carbon surface is in contact with large amounts of CO_2 formed.

It seems that these facts can be explained only on the assumption that the oxygen reacts with chemisorbed carbon oxides, for instance as follows:

$$O_2 + [CO[+ C \rightarrow CO_2 + [CO] \quad (4)$$
$$O_2 + [CO] + C \rightarrow CO_2 + CO \quad (5)$$

and many facts observed in the combustion of carbon are in favour of the hypothesis that these reactions are more rapid than the reaction of oxygen with a clean carbon surface.

According to this hypothesis, carbon dioxide would react exclusively with a clean carbon surface, while oxygen, on the contrary, reacts more readily with surface oxides. This assumption explains satisfactorily the fundamental difference between the interaction of carbon dioxide and of oxygen with carbon. The first reaction is self-inhibiting, while the second is self-accelerating (autocatalytic). Reaction (5) means that oxygen removes the chemisorbed [CO] from the carbon surface, thus accelerating the reduction of the carbon dioxide. This is not a necessary consequence of known phenomena, but from various points of view it seems quite feasible.

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CHEMISTRY

INFLUENCE OF SESQUI-OXIDES UPON THE PROCESS OF FORMATION OF SILICON CARBIDE *

By M. V. KAMENTZEV

(Communicated by I. V. Grebenschikov, Member of the Academy, 8. IV. 1939)

Since the time of Acheson and Fitz-Gerald who were the first to set on foot the manufacture of silicon carbide, the influence of sesqui-oxides upon the process of formation of silicon carbide has been generally considered as highly deleterious. This is usually accounted for by a fall in the temperature of dissociation of silicon carbide (1). The mechanism of the phenomenon in hand is generally assumed to be as follows: oxides are reduced to metals, while the latter are liable to decompose silicon carbide and to form carbides themselves, in course of which process silicon becomes evaporated; with further heating, these newly formed carbides become again decomposed, the metals is driven to the zone of lower temperatures where it once more exercises its detrimental influence, etc.

Brunner (2) and Baur (3) have, however, shown that aluminium carbide evaporates without dissociating, while Prescott and Hincke (4) have found that the formation of this compound commences at 1800°C, i. e. above the temperature at which the pressure of CO in the reaction of $SiO_2+3C=SiC+2CO$ reaches 1 atm. [1470° according to Brunner (2)]. On the other hand, it is generally known that carbide of iron is unstable already at the temperature of SiC formation, while the pressure of iron vapours attains 1 mm only at 1900° C. Analysis of furnace products taken from various temperature zones (Table 1) shows that alumina is liable to sublimation at a temperature which is far from coming close to the point of incipient dissociation of silicon carbide; while iron fails in general to be re-distributed in the furnace.

Table 1

Analysis of Products from Various Furnace Zones for Obtaining Silicon Carbide (at the «Ilyich» works)

Products	SiC	SiO_2	C_{free}	Al_2O_3	Fe_2O_3	CaO	MgO	Approx. t° of layer, °C
Green variegated . . .	92.83	0.85	1.19	0.61	4.19	0.30	0.10	1950—2200
Black coarse-grained . .	90.67	1.81	2.16	1.00	2.80	1.40	0.29	1950—2200
Black fine-grained . . .	88.87	1.15	2.25	2.08	2.52	3.40	0.22	1850—1950
«Amorphous»	87.27	3.05	0.71	4.71	6.49	0.69	0.31	1650—1850
Siloxicon	77.69	6.79	nil	6,05	2.73	1.56	—	1500—1650

* The work was conducted with the participation of Eng. A. T. Dedur.

The above stated leads to doubts regarding the correctness of the existing conception on the mechanism of the influence of sesqui-oxides upon the process of formation of silicon carbide; and these doubts have indeed induced us to carry out the present work.

Experiments in an Acheson Furnace. For the purpose of approaching as closely as possible to industrial conditions, the experiments were performed in an Acheson furnace with a power of 40 kW. Quartz sand from the Zakhojsky Quarry (Station Popovka, October Railway) was used. This sand contained upon washing: 99.8% SiO_2, 0.1% Al_2O_3 and traces of Fe_2O_3. Oil coke with an ash content of 1% was taken (the ash contained 10.0% Al_2O_3 and 19% Fe_2O_3). A 5% excess of carbonaceous material as against the theoretical burden was introduced into the charge according to the equation

$$SiO_2 + 3C = SiC + 2CO.$$

The addition of Al_2O_3 was made in the form of chemically pure alumina, while Fe_2O_3 was introduced in the form of ground «Kalatchev» iron-ore

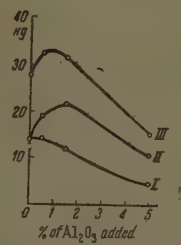

Fig. 1. Yield of product from furnace depending on additions of Al_2O_3.

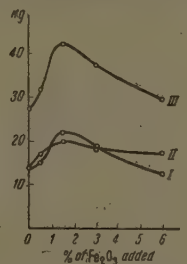

Fig. 2. Yield of product from furnace depending on additions of Fe_2O_3.

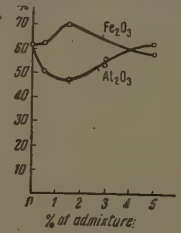

Fig. 3. Yield of SiC (% of theoretical yield) as depending on amount of additions to charge in a Tammann furnace.

containing 96.5% Fe_2O_3 and only 0.1% Al_2O_3. The additions were carefully mixed up with the charge.

All the heats were conducted under the same furnace conditions: duration—24 hours, temperature of core—about 2400°. The results of the experiments are tabulated in Table 2 and represented graphically in Figs. 1 and 2. The curves have the following significance: *I* represents yield of coarse-grained product (which alone is, strictly speaking, the product from an industrial point of view); *II* represents output of fine-grained product (a non-industrial product serving as charge for re-melting) and *III* provides a general conclusion.

As we see, the addition of alumina reduces the yield of coarse-grained silicon carbide at the expense of the output of fine-grained product; the output of the latter

Table 2

Dependence of Yield of Silicon Carbide upon Additions of Sesqui-Oxides to Charge in Experiments with Acheson Furnace

Addition in %		Yield of silicon carbide in kg		
Al_2O_3	Fe_2O_3	Coarse-grained	Fine-grained	Total
—	—	13.9	13.8	27.7
0.5	—	14.0	18.9	32.2
1.5	—	10.2	21.3	31.5
5.0	—	4.4	10.4	14.8
—	0.5	14.7	17.0	31.7
—	1.5	21.9	20.0	41.9
—	3.0	18.8	18.5	37.3
—	6.0	12.6	17.0	29.6

even increases to the extent of 1.5% Al_2O_3 in the charge. At the same time the addition of Fe_2O_3 brings about a growth in the yield of coarse-grained silicon carbide. With the addition of 1.5% Fe_2O_3 the yield of the coarse-grained product constitutes 160% of its output without any additions having been made.

The determination we carried out of the size of crystals of the products obtained with different additions (Table 3), points most manifestly to the detrimental influence of Al_2O_3 and to the beneficial effect of Fe_2O_3 upon the growth of crystals in silicon carbide.

In Table 4 are to be found analyses of silicon carbide (the coarse-grained variety); alumina is almost fully removed from the product, while the content of iron points to there having been no re-distribution of this element in the furnace in course of the process.

The content of free carbon points to there being no increase in the dissociation of SiC with increase of additions, and even shows a decline in the case of the addition of Fe_2O_3.

Table 3

Influence of Addition of Sesqui-Oxides to Charge upon Size of Silicon Carbide Crystals (for coarse-grained product, as established by experiments in Acheson furnace)

Addition in %		Content of grain in %		
Al_2O_3	Fe_2O_3	Larger than 0.35 mm	0.35—0.18 mm	Finer than 0.18 mm
—	—	58.3	39.3	3.8
1.5	—	47.8	46.2	6.9
3.0	—	23.5	62.9	15.7
—	0.5	61.4	34.6	3.9
—	1.5	71.5	24.5	4.0
—	3.0	79.8	17.8	2.4

Mineralogical examination has shown that the grains of silicon carbide from the heats in which alumina additions were made, possess a poorly developed shape, are endowed with a darkish hue and contain many inclusions of inert material from the original charge. At the same time with the addition of Fe_2O_3 the crystals are well-developed and are more often of green than of black colour.

Table 4

Composition of Silicon Carbide Depending on Additions of Sesqui-Oxides to Charge (as shown by experiments in Acheson furnace)

Addition in %		SiC	C_{free}	SiO_2	Al_2O_3	Fe_2O_3	RO
Al_2O_3	Fe_2O_3						
—	—	92.36	4.34	1.51	0.41	0.46	0.28
0.5	—	93.27	2.96	2.36	0.64	0.27	0.21
1.5	—	89.32	4.25	1.12	0.66	0.52	0.67
3.0	—	93.50	4.00	0.48	0.98	0.35	0.38
—	0.5	90.70	5.12	2.11	0.67	0.41*	0.38
—	1.5	91.12	3.20	1.93	0.50	2.78	0.44
—	5.0	89.44	2.81	0.11	0.33	7.17	0.26

Experiments in Tammann Furnace. Experiments in Tammann furnace with a graphite crucible were carried out as a corollary to the experiments conducted in the Acheson furnace and were performed under identical conditions. The same raw materials were applied, but the duration of the experiment was greater, namely 3 hours; 1.5 hour was expended on heating up to 2000° and 1.5 hour for holding at a temperature of about 2200°.

* Sample for analysis passed magnetic separation.

The burden for a single round (37.4 g sand and 49.4 g oil coke + addition) was calculated to yield 50 g SiC. The results of the experiments are summed up in Table 5 and illustrated graphically in Fig. 3.

Table 5

Yield of Silicon Carbide Depending on Additions of Sesqui-Oxides to Charge (as shown by experiments in Tammann furnace)

Additions		Al_2O_3			Fe_2O_3		
in g	in %	Yield in g	Yield % of theoret.	Amount of Al_2O_3 in product in g	Yield in g	Yield % of theoret.	Amount of Fe_2O_3 in product in g
0.0	0.0	30.8	61.6	0.06	30.8	61.6	0.06
0.71	0.5	25.3	50.6	0.08	31.0	62.0	0.55
2.15	1.5	23.3	46.6	0.11	35.0	70.0	1.80
4.26	3.0	27.95	55.9	0.04	26.7	53.4	3.23
7.12	5.0	30.95	61.9	0.18	28.95	57.9	7.15

The effect of Fe_2O_3 additions in these experiments is analogous to that we obtained in our runs with an Acheson furnace. The balance of iron shows that it wholly remains in the product. Iron was identified by us in acid extractions without fusion with SiC. This justifies us in maintaining that iron has its location on the surface of the crystals of silicon carbide, which fact accounts fot the appearance of green crystals even with its content amounting to 17% (calculation made for the metal). Alumina, just as in the experiments with the Acheson furnace, is altogether eliminate from the product; as regards the yields, the picture is rather different: while in the Acheson furnace the yield declined with every increase of alumina content in charge, here we observed first a decline and then a growth in yield. The reason for this seeming contradiction lies in the fact that in the Tammann furnace silica is to a great extent volatilized, which fact, in a considerable measure, accounts for the rather small output of the product. At the same time in the Acheson furnace silicic acid is not removed from the furnace at all. Since the addition of alumina, as we conceive it to be the case (cf. below), by fixing the silica impedes the reaction of formation of SiC, it is clear that loss of silica will decline with increased content of alumina. Yet, at high temperatures when this compound breaks down, silica reacts most vigorously with carbon, which increases the yield of SiC.

Mineralogical examination has shown that with considerable content of alumina, the crystals are fine and of dark colour. At the same time, samples with even the maximum content of iron have well-developed crystals of green colour.

Conclusions

The presence in the charge of oxides of iron ranging up to 2—3% exercises a beneficial influence upon the yield of silicon carbide and contributes to the formation of coarser and more regularly developed crystals. The availability of very considerable amount of iron in the product does not prevent the formation of green crystals. The fact of our having obtained green silicon carbide with an iron content up to 17% is a moment of considerable interest.

Iron introduced into the charge remains completely in the product; it lies almost wholly on the surface of the crystals and can be easily removed by washing with an acid.

The presence of alumina in the charge is found to be objectionable for the process of obtaining silicon carbide. This detrimental effect is particularly manifest in the deterioration of the quality of the product; it notably reduces the yield of the coarse-grained product at the expense of the less valuable fine-grained one. The yield of the latter is even liable to increase somewhat in comparison with the case when a pure charge is taken (up to 1.5—2% of the content of alumina in the charge).

In the presence of alumina silicon carbide acquires the tendency to be crystallized into sword-shaped and thin lamellar grains, i. e. it assumes a form which may be said to be the least advantageous from the point of view of the prospective performance of the product as an abrasive.

Alumina is almost entirely removed from the product, which is apparently due to volatilization.

The results of the present work permit us to assert that the interpretation usually given in the literature to the influence of admixtures (in particular to the effect of sesqui-oxides) upon the process of formation of silicon carbide should be considered as erroneous. Thus, the oxides of iron, instead of the alleged objectionable effect, exert a favourable influence upon the process (of course. within certain limits of their content). The mechanism of this beneficial effect may be understood in conformity with the statement advanced by Prof. I. A. Sokolov ([5]). Metallic iron obtained in result of the reduction of oxides dissolves carbon and thus, by activating it, displaces the equilibrium of the reaction of reduction of silicic acid, and consequently also that of the formation of silicon carbide into the region of lower temperatures, whereby the zone of carbide within the furnace is increased. The beneficial influence of iron may also be explained by the fact that it dissolves silicon producing a considerable positive thermal effect and forming silicide, which factor contributes to the reaction of reduction running its course. The theory of the favourable influence of iron oxides upon the formation of silicon carbide is in good agreement with the conclusions of Prof. M. S. Maximenko and co-workers ([6],[7]) who showed the beneficial effect of iron oxide additions to the charge used for producing calcium carbide, these additions speeding up the rate of formation of the final product.

Alumina is found to have a decidedly objectionable influence upon the process of formation of silicon carbide, yet we cannot agree with the generally accepted understanding of the mechanism involved in this: alumina does not contribute to the dissociation of silicon carbide, but only slows down the reaction of its formation, this being due to the formation of compounds with silica.

The reduction of silicic acid from its compound with alumina is handicapped, wherefore the reaction is liable to slow down and is displaced into the region of higher temperatures, which factor diminishes the carbide zone in the furnace.

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CHEMISTRY

RANGE OF MOLECULAR ACTION OF SURFACES AND POLYMOLECULAR SOLVATE (ADSORBED) LAYERS

By B. DERJAGUIN, M. KUSSAKOV and L. LEBEDEVA

(Communicated by Wl. A. Kistiakowsky, Member of the Academy, 2. IV. 1939)

In a series of papers on the abnormal properties of thin liquid layers begun by one of us as far back as 1931 (1), were quoted experimental evidences of a large radius of action of surface forces and peculiar properties of polymolecular layers differing from the properties of the phase. This question was furthermore a subject of discussion on the pages of «Nature» (2). The experiments described below, even in that part which had been exposed in detail in a paper published over a year ago (3), afford in our opinion a very demonstrative and convincing solution of the problem under consideration (4).

We have shown by direct measurements (3) that the thickness h of a film formed by a wetting liquid between a gas bubble and a solid surface is a function of the excessive capillary pressure, $P=\frac{2\sigma}{r}$, prevailing within the bubble (r is the radius of the bubble and σ is the surface tension of the liquid). P is, as it were, counterbalanced by the «disjoining action» of the thin film, conversely, $P=P(h)$. One of the numerous photomicrographs of the interference patterns, obtained for a water film on mica, is shown in Fig. 1. The central black spot corresponds to a film thickness of about $1.2\cdot10^{-5}$ cm. The relation between P and h observed for the same system is represented in Fig. 2 by circles on a solid curve. The values of h measured correspond to thermodynamically equilibrium states which may in particular be inferred from the fact that the same values of h were obtained irrespective of whether they were reached by reducing the thickness of a thicker film or by increasing that of a thinner one. It follows that the range of action of molecular surface forces is at least equal $2\cdot10^{-5}$—$3\cdot10^{-5}$ cm. It may be theoretically shown that a wetting film is stable when $\frac{\partial P}{\partial h}<0$. For a number of aqueous solutions, the wetting film while exhibiting a stability region at greater thicknesses collapses at a smaller thickness (and at greater pressures) leaving a film too thin to be measured interferometrically and ultimately forming a contact angle of 1—3° in the case of electrolytes and ca. 50° in the case of an aqueous solution of *p*-toluidine on mica. This testifies to a relation of the type represented in Fig. 2 by a dotted line which for thicknesses corresponding to a certain region where $\frac{\partial P}{\partial h}>0$ corresponds to absolutely unstable states. As may be readily shown, such a form of the P, h graph accounts for the hysteresis of wetting.

Independently of these experiments conducted in our laboratory, the existence of an upper limit of thickness of stable wetting layers of liquids was suggested by A. Frumkin (5) who worked out a theory of incomplete wetting on this basis.

Dissolved substances may not only change the stability of the wetting film at small thicknesses, but also radically alter the form of the whole P, h curve, in particular for large values of h; they may either raise or lower the curve as a whole. The lowering is to be observed for aqueous solutions of electrolytes at sufficient concentrations (0.01 and 1.00 N) on mica, glass

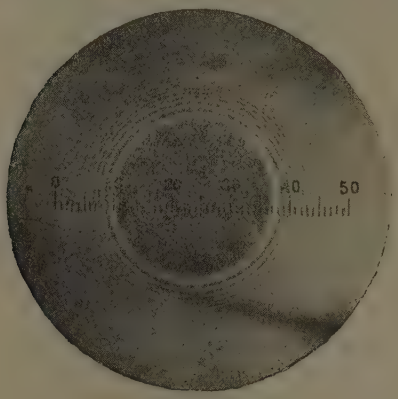

Fig. 1.

Fig. 2.

and quartz and in the case of p-toluidine solutions on mica; a rise of the P, h curve takes place for aqueous solutions of sugar on mica, oleic acid solutions in non-polar hydrocarbons on steel, glass and quartz and 0.1 N solution of LiCl on a polished diamond facet (in the latter case the thickness of a layer under a pressure of 900 dynes/cm² increases from $0.25 \cdot 10^{-5}$ cm for pure water to $0.75 \cdot 10^{-5}$ cm for solution).

It may be shown thermodynamically that the variation of h with the concentration of the solute (for $P = \text{const}$) is incompatible with the assumption of the unimolecular nature of the adsorbed layers on both surfaces of a film of the solute. Our experiments thus prove the diffuseness (of the order of 10^{-5} cm) of adsorption layers at solution—solid interfaces for electrolytes as well as non-electrolytes.

It is essential to note that at any rate within the scope of the Debye-Hückel theory the existence of the pressure P in aqueous solutions cannot be completely accounted for by electrostatic interaction of diffuse ionic layers* bound to both surfaces of the film. Thus, the thickness of a film of 0.1 N aqueous solution of LiCl on a polished diamond facet proved to be $0.75 \cdot 10^{-5}$ cm at a pressure $P = 900$ dynes/cm², whereas the thickness of dif-

* A mathematical theory of the forces arising in the case of interaction of two such layers (belonging to two identical interfaces) was developed by one of us in 1935 (6). The calculations being applied to the question of the stability of lyophobic colloids and to the determination of the critical value of ζ-potential, only the approximate theory relating to the case of small ζ-potentials was published.

Similar results are to be found in a paper by P. Bergmann, P. Löw-Beer and H. Zocher (7) devoted to the theory of the Schiller layers. These calculations hold for large ζ-potentials also; however, in contradistinction to the case discussed in our paper, it is assumed that not ζ-potentials, but the charges on the surfaces are constant. An extension of analogous calculations to the case of wetting films is given in a paper by A. N. Frum-

fuse ionic layers in this solution ought to have been ca. 10^{-7} cm, so that these layers could not have interacted to any appreciable extent being divided by a distance of 10^{-5} cm.

The effect observed can neither be put down to the van der Waals, e. g. London's dispersion attraction forces which obey the «additivity» principle. This is evidenced by the experiments on 0.1 *N* solution of LiCl just referred to, as well as by the total disappearance of the effect (perhaps reversal of the sign of *P*) in the case of water on mica or glass as a result of covering the solid surface by a monolayer of either calcium stearate [by the method of Blodgett-Langmuir ([11])] or paraffin. The effect seems to be associated with the orientation or polarisation of the molecules being extended from the surface of the solid into the depth of the liquid. It is but natural that the presence of a foreign monolayer on the surface of the former (e. g. in the case of adsorption) may change the effect altogether.

The disjoining action of liquid films between identical surfaces which had been studied in our laboratory at a still earlier date, may afford a basis for a theory of slow coagulation and stability of colloids and dispersoids, sorption by porous substances ([12]) and also for the theory of many other phenomena.

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kin ([8]), in which the case of the wetting film bearing no charge on its outer surface was also discussed.

In 1938 I. Langmuir published a paper ([9]) containing similar calculations with detailed analysis of the case of large ζ-potentials (for small ζ-potentials, the calculations of all the four authors concide). It may be concluded from this paper that the author was, unfortunately, not acquainted with some of the investigations mentioned above. On the basis of his calculations Langmuir assumes the existence of wetting films of dilute aqueous solutions of electrolytes on solid surfaces and gives the values of their thickness under various conditions (pressures), applying this conclusion also to the explanation of the Jones-Ray effect ([10]). However, our direct measurements([3]) of the thickness of wetting films have proved the existence of thick wetting films in a considerably greater number of cases (almost in all cases of complete wetting of one phase by another), and not only for dilute aqueous solution of electrolytes.

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CHEMISTRY

ISOTOPIC COMPOSITION OF RAIN WATER

By R. V. TEISS

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Very few indications concerning density and isotopic composition of rain water are to be found in literature. While the density of snow water has been measured by many authors, very similar results being obtained, rain water has been the object of experimental investigation only in two papers.

In this paper the author compares data on densities of rain water samples for rains of different character, the samples having been taken mainly in summer 1937, in Moscow (except one sample of rain water which was taken at the Black Sea coast at Gagry).

The samples of rain water were purified by using the methods suggested in the paper by H. J. Emeleûs, F. W. James, A. King, F. G. Pearson, R. H. Purcele and H. V. A. Briscoe (4), with the only difference that all stages of the purification process were carried out in quartz vessels and that after the distillation from potassium permanganate an additional distillation was introduced. The Moscow tap-water, taken as a standard (on January 29, 1938) was purified in the same way. Both waters, previous to measurements, were freed from dissolved air by boiling in a vacuum. For density determinations the method of flotation was adopted and a float of fused silica was used. The authors used this method with the modifications introduced by E. S. Gilfillau (5), i. e. the flotation pressure was measured at a constant temperature of 0°. The float of fused silica having a volume of about 0.5 cm^3 was shaped like a buoy, as the one described in detail by Richards and Shipley (6), but contained no mercury inside. The exact value of the flotation pressure was found in the following way: at first the author determined approximately the point where the direction of motion of the float was reversed, and then the velocity of this motion was determined a little higher and a little lower than the point of reversion. The interval within which the velocity was measured, was mostly 10 mm (sometimes 5 mm). The exact value of the flotation pressure was calculated from these two figures. The final flotation pressure was calculated as an average from at least 3—5 observations.

In order to pass over from the flotation pressure to the differences in density, the float was calibrated in potassium chloride solutions, the density of which were calculated according to the formula given in the same paper by E. S. Gilfillau. This calibration necessitating so small samples of the chloride that it would have been impossible to weigh them even on a microscale, a solution of potassium chloride in standard water (0.834 mg/cm^3) was prepared and all other solutions were prepared by weighing samples

of this solution by means of a quartz microburette into a weighed amount of water. In this manner a series of potassium chloride solutions was prepared and the difference between the flotation pressure in these solutions and in standard water was determined. A curve was plotted which enabled the transition from flotation pressures to the corresponding differences in density. For waters lighter than the standard the float was calibrated by means of a similar series of solutions of potassium chloride in a water having the smallest density (in snow water). The negative value of the density of this water was determined in a chloride solution in this water, the flotation pressure of which was near to that of standard water.

The densities of rain waters differ only slightly from the standard. All of the values may be plotted on the calibration curve of the float within the interval where the sensitivity of the float is 0.17 γ.

An essential condition of the precision of the density comparisons is the constancy of the temperature at which the flotation pressure is determined. The quartz vessel which contained the water, the density of which was to be determined, was immersed in a silvered Dewar vessel filled with a mixture of distilled water and ice prepared from the same water. The motion of the float was observed through a transparent stripe in the Dewar vessel. It should be noted that the temperature of such a mixture of water and ice is very far from ideal constancy. Fluctuations may amount to a few hundredths of a degree and this can lead to considerable errors in the determination of density, particularly in the case of samples of water differing only little from the standard. By this reason the course of temperature changes of the mixture of ice and water was preliminarily determined. As a rule, the temperature did not settle immediately after the preparation of the mixture, but after 30—40 min. An example of the temperature changes in such a mixture is given below. The temperature was determined by means of a Beckmann thermometer having a range of 5° and graduated in 0.01°. The thermometer was set so that 0.00° corresponded to 2.340° of the Beckmann thermometer.

11 h. 1 min.	2.332°	12 h. 51 min.	2.340°
11 » 11 »	2.332	1 » 41 »	2.340
11 » 36 «	2.334	2 » 41 »	2.341
11 » 51 »	2.338	3 » 51 »	2.342
12 » 21 »	2.339	5 » 31 »	2.343

Thus, from the beginning of the experiment, in the course of 6.5 hours, the temperature has changed by 0.01°. After 50 min. from the beginning, a temperature was reached which to the end of the experiment had changed only by 0.005°. It is possible to maintain within two hours a temperature within 0.001—0.002°. The constance of the temperature of the mixture depends mainly upon the structure of the ice prepared from distilled water. A compact transparent ice prepared by slow freezing gives a temperature which is lower and more constant compared with not very transparent vesicular ice which one obtains by a quick freezing of the water. When determining the flotation pressure, it is necessary to control continuously the constancy of the temperature by means of the Beckmann thermometer. But besides the constancy of temperature during one experiment, it is essential to obtain an identical temperature in a whole series of determinations. This is not always easily achieved and a deviation from this rule may lead to considerable errors, particularly in the case of waters having a density that approaches the standard. It was possible to overcome this difficulty, since in the determination of density it is not the absolute value of the flotation pressure that matters, but the difference between the flotation pressure of the water investigated and that of the standard water. Therefore it is important to deter-

mine the densities of both samples without taking care of the temperature being constant during a whole series of experiments. Thus, a repeated determination of the standard water under given conditions makes it possible to obtain exact results even in the case of waters having a very small difference in density. When the above conditions were observed with the sensitivity of the float being 0.17 γ, the average error of the determination did not exceed 0.3 γ. The compressibility of the quartz float was less than that of water: with increase of pressure the float rose, with decrease of pressure it sank.

The variations in the density of rain water measured by this method are given in Table 1. The density of water samples from three thundershowers two of which were taken in Moscow on April 15 and 28, 1937, and one in Gagry on September 19, 1937, was determined.

The data of Table 1 are an average of five determinations. The 2nd and 3rd sample were determined a second time after an additional distillation. Concurrent results were obtained.

Table 1

Date and place of the taking of the sample and character of the rain	Difference in density, γ
Thunder-storm rain, May 15, 1937, Moscow	+ 2.7
Rain with hunder-storm and hurricane, May 28, 1937, Moscow*	+ 2.7
Rain with thunder-storm at the Black Sea coast (Gagry), September 19, 1937	+ 2.1

The samples reported in Table 2 are of another kind. All these samples were taken in Moscow on the same day, July 7, 1937. They were samples of different non-thunder-storm rains taken on a rather cold day. It was raining intermittently the whole day. All these rains were of one kind: at first, the rain was fine, then it became driving, with large drops and was accompanied by a strong wind. In the last sample we succeeded in dividing these two stages—the first and the following one.

Table 2

Time of the taking of the sample	Volume of sample, cm^3	Difference in density, γ
2 rains, samples taken together, between 13 and 14 hours**	—	— 1.2
After 14 h.***	—	— 1.0
Between 18 and 19 h.		
I part****	20	+ 1.2
II part	100	— 1.4

* Rain with hurricane described in «Izvestia», May 29, 1937. The main part of the rain accompanied by a thunder-storm and hurricane was collected. The second part of the rain after the thunder-storm could not be collected, the rain being very feeble.

** 3rd and 4th rain on the day of July 7, 1937.

*** 5th rain.

**** 8th rain.

All these rains have almost the same density. The average density of the last rain calculated from the data obtained is almost —1.0 γ.

By comparing these two rains it may be seen that the density of water from thunder-showers differs considerably from that of non-thunder-storm rains. Moreover, the data obtained for the two samples of the last rain confirm the fact pointed out by M. Harada and T. Titani[2] who found that the first portions of a rain have a density that is higher than that of the following portions. As a further confirmation of the difference in density existing between thunder-storm rains and non-thunder-storm rains, a series of rains is given in Table 3. The samples were taken in the evening on July 2, 1937. During that evening there have been many rains, all of them different.

Table 3

Character of the rain	Time of its falling	Difference in density, γ
Rain with thunder-storm and hail	From 18 h. to 18.20	+0.5
Part of the same rain, during the fall of the hail*	18.05—18.10	+0.1
Thunder-storm rain (first half) .	19.20—19.40	+2.7
Rain without thunder-storm . .	20.45—21.15	−0.9

All these rains had been falling during three hours on the same evening, and according to the synoptic data of the Central Institute of Weather they were called forth by a common cause—the passage along the western frontier of the USSR of a front separating continental tropical air from the previously prevailing marine air of polar origin. Notwithstanding their having fallen on the same evening, the density of these rains differs considerably depending on the fact of their being or not accompanied by thunder-storm phenomena. The density of the first (thunder-storm) rain (the sample of water contained also hail) was higher than that of the standard water, but lower than that of the two other thunder-storm rains (Table 1), probably because of the lesser density of hail. This point of view is confirmed by the second figure of Table 3 expressing the density of a mixture of hail and rain water, the sample being taken at the time of the falling of the hail. To check this assumption, a sample of hail that had fallen on July 13, 1938, was taken. The hail was separated from rain water, the water obtained after the melting of the hail was subjected to purification and its density determined. The value for hail-water was found to be —1.5 γ.

Table 4 shows the density of one long rain. The rain fell during 7 hours without intervals on August 20, 1937, which was a rather cold day. The samples were taken one after another.

Table 4

Parts of the rain	Time of the taking of the sample	Volume of sample, cm^3	Difference in density, γ
1	12 h.—13.15	75	+0.4
2	13.15—14.30	150	−2.3
3	14.30—15.45	75	−2.3
4	15.45—18.15	60	−2.3
5	18.15—19.15	40	−0.3

* The density is equal to the density of the standard: the figure is within an experimental error.

The average density of this rain calculated from these data was found to be —1.6 γ. The relation between different parts of the rain pointed out by M. Harada and T. Titani was observed at the beginning of the rain. Towards the end it was disturbed.

Thus, the data of all the four tables give a negative value for non-thunder-storm rains, while water from thunder-storm rains was found to be heavier than standard water. No conclusions can be drawn concerning the cause of this phenomenon on the basis of facts we dispose of. It is reasonable to suppose that this is the result of an activation by thunder-storm phenomena of exchange reactions between the oxygen of the water in clouds and atmospheric oxygen which is heavier than the oxygen of water ([8]). In the literature we find indications considering the possibility of such an exchange taking place in the atmosphere ([7]). From the fact that the difference in density of non-thunder-storm rains is nearer to the one calculated theoretically, it is only possible to make the conclusion that the water of these rains is being subjected to lesser changes in the atmosphere and that the comparatively higher density of water from thunder-storm rains has been the result of some deeper changes in the isotopic composition.

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CHEMISTRY

EFFECT OF THE NATURE OF THE SOLVENT UPON THE PROCESS OF ELECTROCRYSTALLIZATION OF SILVER

By E. S. SARKISOV

(*Communicated by Wl. A. Kistiakowsky, Member of the Academy, 31.III. 1939*)

In the present paper one of the factors determining the process of the electrolytic separation of metals is investigated, viz., the dependence of the change in the number of crystal centers (nuclei) originating on the cathode surface upon the nature of the solvent.

A study of the formation of crystalline silver centers from non-aqueous solutions is of particular interest, because up to the present practically no one has undertaken to clear up this problem. It should be noted that a great number of papers (1) have appeared on the electrolytic precipitation of silver from non-aqueous solutions, which deal mainly with polarization phenomena. As regards the structure of the silver precipitates which separate from non-aqueous solutions, these papers contain only scattered information dealing with the character of the precipitates obtained as a function of the current density (2).

The change in the number of crystal centers was studied in the initial process of the electrocrystallization of silver from an aqueous solution of $AgNO_3$, from dehydrated alcoholic solutions of $AgNO_3$ (methyl and ethyl alcohols), and from a pyridine solution of $AgNO_3$. Silver was selected as the object of this investigation because under suitable conditions individual monocrystals of silver which may be easily counted with the aid of a microscope ($\times 120$), are deposited on the cathode surface from a solution of silver nitrate. A direct count of the number of crystals originating and growing on the cathode surface makes it possible already at the initial moment of the electrocrystallization to find a quantitative dependence of the number of crystal centers originating upon the nature of the solvent (3).

In this investigation a statistical method of counting the number of crystals formed was employed in order to escape those deviations which, as a rule, occur during the electrocrystallization of metals, even if the experiments are carried out with great care. To determine the number of crystalline centers with greater precision, we carried out the experiments at a constant potential of 30.2 mV between the electrodes, because when the voltage is constant, the number of crystalline centers that have once appeared on the cathode remains constant throughout the experiment (3). This phenomenon is explained by the appearance of those obstructing factors which accompany the formation of the first metal nuclei (4).

In the experimental part of the investigation a great deal of attention was paid to thorough purification of the electrolytes and thorough cleaning of the electrodes from the slightest impurities. Special care was necessary in carrying out the experiments because, as preliminary experiments showed, artificially introduced admixtures distorted the real picture of the phenomenon of electrocrystallization, in some cases masking the effect of the nature of the solvent.

The electrolysis was carried out in a cylindrical glass vessel 90 cm^3 in volume (Fig. 1). In the upper part of the cylinder there was an opening 2—3 mm in diameter opposite the cathode. This opening made it possible to directly count, with the aid of a microscope, the number of crystalline silver centers forming. The cross-section of a platinum wire 1 mm in diameter, tightly sealed into a glass capillary, served as a cathode. This cathode, with the aid of a special ground joint, was introduced into the glass cylinder through the lower opening of the vessel. Such a construction of the cathode made observation of the eletrocrystallization process easier and at the same time enabled one to carry out the process under better controlled conditions. A ring of thin plate silver, sealed into the side wall of the vessel, served as an anode and was concentrically located with respect to the cathode. Thus, in all the experiments the distance between the anode and the cathode was constant.

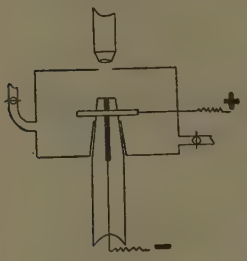

Fig. 1.

The electrolytic solution was prepared from silver nitrate which had been preliminarily heated in air to remove organic matter and then was recrystallized several times. In order to study the effect of the nature of each individual solvent upon the electrocrystallization of silver (in all experiments a 0.25 *N* solution of $AgNO_3$ was used), 40 experiments were carried out. Each series of experiments with a given solvent was run without interruption. All organic substances used as solvents were subjected to preliminary distillation immediately before the start of an experiment.

Table 1 contains the data on the formation of crystalline silver centers from a 0.25 *N* $AgNO_3$ solution; these data were obtained in experiments with various solvents; furthermore, in this table the per cent of probability of the formation of a given number of crystalline centers is also presented.

Table 1

Probability of the Formation of Crystalline Silver Centers (in %) from a 0.25 *N* Solution of $AgNO_3$

Solvent	Number of crystalline centers forming																					
	8	9	10	11	12	13	14	21	22	23	24	25	26	27	33	34	35	36	37	38	39	40
H_2O	—	2.5	10	67.5	12.5	7.5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
CH_3OH . .	—	—	—	—	—	—	—	—	5	10	12.5	55	10	7.5	—	—	—	—	—	—	—	—
C_2H_5OH . .	—	—	—	—	—	—	—	—	—	—	—	—	—	—	2.5	5	15	45	12.5	12.5	5	2.5
C_5H_5N . . .	An exceptionally finely crystalline precipitate																					

An analysis of Table 1 leads to the following conclusion: the number of crystalline silver centers originating during electrocrystallization depends

upon the nature of the solvent. Thus, for example, if for an aqueous $AgNO_3$ solution the most probable number of crystalline silver centers forming (n_z) is 11, i. e., the probability of the formation of 11 crystals under the given conditions of the electrolysis is a maximum and is equal to 67.5%, then for methyl alcohol $n_z = 25$, and for ethyl alcohol $n_z = 36$. When pyridine was used as the solvent, silver separated out on the platinum cathode not in the form of isolated monocrystals, but in the form of an exceptionally finely grained precipitate (Fig. 2) similar to that which is formed during the electrical precipitation of silver from a solution of the complex cyanide.

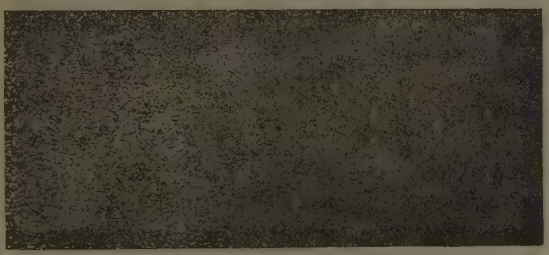

Fig. 2.

It is necessary to take note of the fact that the separation of silver from the pyridine solution did not occur at the voltage 30.2 mV used in the case of water and methyl and ethyl alcohols, but a higher voltage equal to 68.7 mV was necessary for the separation of silver to start.

A very interesting relation is observed upon a comparison of the values of the most probable number of crystalline silver centers formed (n_z), obtained from the first three solvents (H_2O, CH_3OH, and C_2H_5OH), with their dielectric constants *(D)*. In all the cases presented the product of n_z multiplied by the corresponding value of the dielectric constant of the solvent is a constant, i. e.,

$$D_{H_2O}\, n_z^{H_2O} = D_{CH_3OH}\, n_z^{CH_3OH} = D_{C_2H_5OH}\, n_z^{C_2H_5OH} = \text{const.}$$

Data illustrating this dependence are presented in Table 2.

Table 2

0.25 *N* $AgNO_3$

Solvent	n_z	D	$n_z \cdot D$	Note
H_2O	11	81.7	898.7	The values for D were borrowed from Walden [5]
CH_3OH . .	25	35.4	885.0	
C_2H_5OH . .	36	25.4	914.4	

The regular increase in the number of crystalline silver centers (n_z) forming on the cathode as a function of the dielectric constant of the solvent, which was established in the given case, may be explained by the different ability of the solvents to form complex salts with $AgNO_3$. The stability and the number of complex ions will be different depending upon the nature of the solvent.

It is known that in the case when $AgNO_3$ is dissolved in a number of solvents, the concentration of silver nitrate being the same in each, the solution formed contains the greater quantity of complex ions $Ag(NO_3)'_2$, the smaller the dielectric constant of the solvent ([6]). From this it follows that the complex ions, with a decrease in the value of the dielectric constant of the solvent, become more and more important. Due to this the number of crystalline silver centers should increase, since it is known that from solutions of complex compounds metals are deposited on the cathode in a finely crystalline form.

Indeed, the data of our investigation confirm the above statement: the increase in the number of crystalline silver centers (n_z) occurs in the following increasing order:

$$n_z^{H_2O} < n_z^{CH_3OH} < n_z^{C_2H_5OH} < n_z^{C_5H_5N}.$$

Here a dependence for the first three solvents can be expressed in the form: $n_z.D = \text{const}$. The deviation of pyridine from this regularity is probably connected with the relatively greater affinity of pyridine for $AgNO_3$ molecules. Thus, it has already been established by Kahlenberg and Brewer ([7]) that there exist very stable complex compounds of $AgNO_3$ with three and two pyridine molecules ($AgNO_3.2C_5H_5N$ and $AgNO_3.3C_5H_5N$).

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PHYSICAL CHEMISTRY

PLASTICITY OF POLYCRYSTALLINE SOLID SOLUTIONS OF METALS

By JACOB B. FRIEDMANN

(Communicated by N. S. Kurnakov, Member of the Academy, 29. III. 1939)

1. Metallic solid solutions constitute the basis of most technical alloys, and therefore a study of the laws of the change in the mechanical properties as a function of the composition of the solid solution is extremely important for physical metallurgy.

A similar regularity for the resistance of solid solutions to plastic deformation was established by N. S. Kurnakov and S. F. Zhemchushni (1). The resistance to plastic deformation (Brinnell hardness) for a solid solution is always greater than that for a pure metal. It is also extremely important to ascertain the similar dependence of the influence of the composition on the plasticity of a solid solution. Current opinions are very contradictory, which is partly explained by the choice as a criterion of plasticity of such properties which often change conversely [relative elongation (δ%), reduction of the area (ψ%), and others].

On the basis of the work of Sachs (2) and Kuntze (3), it can be considered as established that per cent elongation (δ%) which mainly points to the uniform deformation, is not a criterion for the maximum plasticity. Therefore, selecting contraction of the area (ψ%) as the criterion for the maximum (static) plasticity, in the present investigation there are discussed certain regularities of the influence of the composition upon the plasticity of solid solutions.

Here we divide all polycrystalline solid metal solutions (depending upon the plasticity of the basic metal at low temperatures) into two fundamental groups:

a) Solid solutions with Ni, Cu, Ag, Al and other face-centered metals as a basis which do not show cold brittleness at the very lowest temperatures.

b) Solid solutions with iron, magnesium, and other metals as a basis which, at a temperature lower than a definite fixed temperature interval, pass over into a brittle state (cold brittleness).

2. Solid solutions with copper, silver, aluminium and other metals as a basis which do not exhibit cold brittleness are less plastic than the pure metals (4).

However, a number of exceptions are known. Thus, for example the technical alloy Cu—Zn (brasses) and Cu—Sn (bronzes) surpass pure copper plasticity (5).

Fig. 1a clearly shows that the decreased plasticity of technical copper, in comparison with solid solutions, is explained only as due to impurities in the copper. The reduction of area (ψ%) in the pure solid solutions Cu—Zn, Cu—Al, Cu—Sn and others always decreases with an increase in the concentration (6).

The cause of such a sharp difference between technical and pure copper lies possibly in the presence of impurities, in particular of oxygen which markedly lowers the plasticity of copper (6).

In alloys this injurious action of oxygen and other impurities is weakened by the deoxidizing effect of the components (Zn, Al, Sn), and therefore the difference between technical and pure solid solutions is very much less than between technical and pure copper.

Consequently, the general rule of the lowering of the plasticity of solid solutions, formed with such base metals which do not exhibit cold brittleness, also ought to be considered as corroborated for the systems Cu—Zn, Cu—Al, and Cu—Sn if the alloys are sufficiently free from impurities.

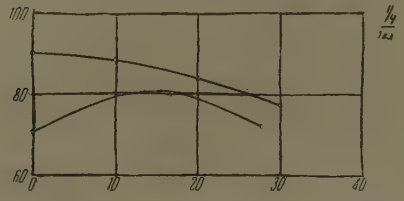
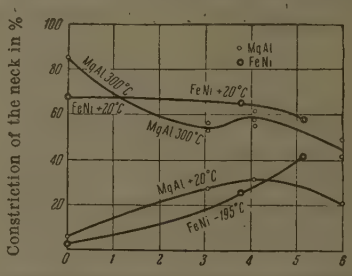


Fig. 1a. Solid solutions with base metals which have no cold brittleness. Lower curve—technical alloys according to Körber-Rohland (5). Upper curve—very pure alloys according to Broniewski (6).



Concentration of solid solution in weight %

Fig. 1b. Solid solutions with cold brittle metals as a basis, according to the data of J. B. Friedmann and M. S. Denisova.

Fig. 1. Influence of the composition upon the plasticity of annealed polycrystalline solid solutions.

3. An essentially different picture is obtained for solid solutions when metals (Fe, Mg) which exhibit cold-brittleness are used as a basis. As is known, these metals give a sharp decrease in the plasticity (7) below a definite temperature intervals (critical temperature).

Below the critical temperature (which lies about +225°C for magnesium during static tests, and about —120°C for iron), additions which form a solid solution may greatly increase the plasticity [contraction in area (ψ%) of the basic metal] (Fig. 1b). This increase in plasticity, as an investigation carried out by the writer in collaboration with M. S. Denisova showed, occurs due to the marked increase in resistance to cohesion.

Since cold brittleness is not removed with a decrease in the amount of impurities and is observed even in the case of extremely pure magnesium, iron, cadmium, beryllium (7,8) etc., it ought to be considered that in these cases we have, as a rule, a marked increase in the plasticity of the solid solution with an increase in the concentration*.

Above the critical temperature of brittleness we have a decrease in the plasticity with the concentration in these systems, too (Fig. 1b).

For the Mg—Al alloys it is also established, by analogy with the previously known relations for Fe—Ni alloys (7), that the temperature interval of the plastic state expands with an increase in the concentration of the solid solution (Fig. 2). At 120°C the angle of bend at which fracture begins for the solid solution Mg+4% Al is about 180°; for magnesium this angle at the same temperature is considerably smaller (Fig. 2).

The phenomenon pointed out has been used for a long time in metallurgy for obtaining relatively plastic iron and magnesium alloys, steels, plastic

* This, however, is not correct for monocrystalline solid solutions in the system Mg—Al upon a measurement of the crystallographic slip in the basis plane (9).

at temperatures below 0°C (Fe—Ni) and magnesium alloys with an increased plasticity (Mg—Al). Further study of the plasticity of various solid solutions on the base of Mg and Fe should lead to the development of new plastic magnesium and iron alloys.

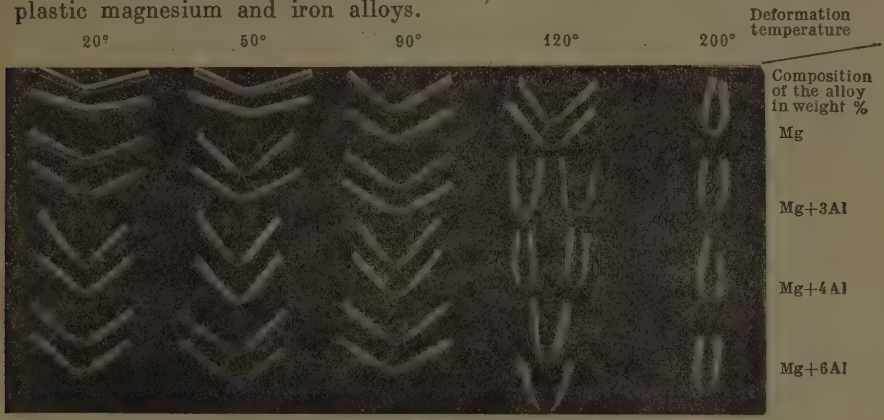


Fig. 2. Increase in the plasticity at solution of aluminium in magnesium (static bend at the temperatures pointed out in the figure) according to the data of J. B. Friedmann and M. S. Denisova; the bend up to the appearance of the first fracture. At 200° C all alloys may be bent∼180°. At 120° Mg+4% Al still has approximately the same plasticity. Pure Mg already begins to pass over in the region of cold brittleness. The alloy Mg+ +6% Al is more brittle than the alloy Mg+4%Al due to the heterogeneity of the former alloy.

Conclusions

a) In the present paper, on the basis of [2] and [3] the reduction of the area (ψ%) and not the relative elongation (δ%) is considered as a criterion of the maximum static plasticity, in particular in estimating the plasticity of metallic solid solutions.

b) The plasticity (reduction of area ψ%) of pure solid solutions with such base metals which do not exhibit cold brittleness (Cu, Al and others) always decreases with the increase in concentration. The presence of anomalies in the systems Cu—Zn and Cu—Sn is explained by the marked effect of impurities (oxygen and others) on the plasticity of copper.

c) The plasticity (reduction of area ψ%) of pure polycrystalline solid solutions with such base metals which exhibit cold brittleness (magnesium, iron), markedly increases in the temperature region of cold brittleness with an increase in the concentration. In such alloys the temperature interval of the plastic state widens also.

At high temperatures plasticity in these solid solutions (Fe—Ni, Mg—Al) decreases with an increase in the concentration.

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PHYSICAL CHEMISTRY

ACTIVATION ENERGY AND ENTROPY OF THE TRANSITION STATE

By J. K. SYRKIN and M. A. GUBAREVA

(Communicated by A. N. Frumkin, Member of the Academy, 15.IV.1939)

It has been repeatedly pointed out (1) that in the Arrhenius equation for the rate constant

$$k = Ae^{-\frac{E}{RT}} \qquad (1)$$

a certain relation

$$k = Be^{\frac{E}{C}}e^{-\frac{E}{RT}} \qquad (2)$$

exists between A and E. According to the theory of the transition state, the rate constant for a gaseous reaction is equal to

$$k = \frac{kT}{h}e^{\frac{\Delta S_g^*}{R}}e^{-\frac{\Delta H_g^*}{RT}} \qquad (3)$$

where ΔS_g^* is the difference in entropy between the transition and the initial state. From equation (2) it follows that a linear relation exists between the activation energy ΔH_g^* and the entropy ΔS_g^*:

$$\Delta S_g^* = \alpha \Delta H_g^* + \beta. \qquad (4)$$

Recently an equation of the type of (4) has appeared in the works of a number of investigators, generalized and applied to various cases, i. e., to the solubility of gases, liquids and solids (2).

Thus, for example, after an examination of the empirical expression for the solubility of one substance in different solvents

$$\ln x = -\frac{\Delta H}{RT} + b \qquad (5)$$

(where x is the solubility in molar fractions), Evans and Polanyi showed that the connexion between ΔH and b $\left(\text{where } b \text{ may be expressed as } \frac{\Delta S}{R}\right)$ may be represented by equation (4).

Actually, in all the cases of solubility examined in this paper, there is absolutely no necessity for the selection of the two constants α and β. Experimental data are very well described by the equation;

$$\ln x = \frac{\Delta H}{R\theta} - \frac{\Delta H}{RT} \qquad (6)$$

where ΔH is the heat of solution and θ is the melting point of the dissolved substance. In the case of an ideal solution, ΔH would be equal to the heat of fusion of the dissolved substance. The applicability of equation (6) signifies that the solution happens to be regular according to Hildebrand's definition or that it behaves as an ideal solution, but with an altered heat of fusion.

It is of interest to ascertain the applicability of equations (2) and (4) to the cases of the kinetics of reactions taking place in different solvents, with rates which differ markedly from each other and with a large difference in the energies of activation and in the pre-exponential factor.

Instead of the equation (3), we have

$$k = \frac{kT}{h} e^{\frac{\Delta S_g^*}{R}} e^{-\frac{\Delta H_g^*}{RT}} \frac{f_1 f_2}{f_3} \quad (7)$$

for the rate constant in solution, where f_1, f_2 and f_3 are the corresponding distribution coefficients of the initial substances and of the transition state between the gaseous and liquid phases. We take note that

$$\frac{f_1 f_2}{f_3} = \frac{n_3}{n_1 n_2} \quad (8)$$

where n is the corresponding volume solubilities.

The distribution coefficient f may be represented by the following equation:

$$f_1 = e^{\frac{\Delta S_1}{R}} e^{-\frac{\Delta H_1}{RT}} \quad (9)$$

and if relation (4) between ΔH_1 and ΔS_1 holds for one substance in different solvents, then for the rate constant of one reaction in different solvents we should get (if $\alpha_1 = \alpha_2 = \alpha_3$)

$$k_{sol} = \text{const}\, e^{\frac{\alpha \Delta H^*}{R}} e^{-\frac{\Delta H^*}{RT}} \quad (10)$$

where ΔH^* is the activation energy which is observed in the given solvent.

We studied the kinetics of the Menshutkin type reaction between dimethyl aniline and ethyliodide in benzene, ethyl alcohol and in mixtures of these two substances. The concentrations of the starting substances were about 0.48 mol per litre. Measurements were carried out at the three temperatures 35, 45 and 55°C. The experiments carried out in pure benzene are not very accurate, since the solubility of the salt formed is very slight and a precipitate begins to form. Each experiment was repeated two to three times. The constants obtained agree very well. The data obtained are presented in Table 1 which shows the composition of the solvent in mol fractions, the rate constants at the three temperatures, the energies of activation and the pre-exponential factors.

Table 1

Solvent		$K_{35} \cdot 10^5$	$K_{45} \cdot 10^5$	$K_{55} \cdot 10^5$	ΔH	A
C_2H_5OH	C_6H_6					
1.0	0.0	0.350	0.868	1.99	17 400 ± 250	$10^{9.91}$
0.60	0.40	0.265	0.62	1.37	16 480 ± 50	$10^{8.18}$
0.34	0.66	0.156	0.351	0.704	15 080 ± 700	$10^{8.015}$
0.075	0.925	0.055	0.111	0.204	13 120 ± 450	$10^{3.065}$
0.0	1.0	0.0246	0.0442	—	11 400	$10^{1.49}$

In the reaction studied, the rate constant in benzene is 20 times smaller than that in alcohol. The energy of activation upon passing from alcohol to benzene decreases by 6000 cal. and the pre-exponential factor becomes 300 000 times smaller. Although the reaction should proceed faster with

a decrease in the energy of activation, actually just the opposite is observed due to the faster decrease in the pre-exponential factor. The course of the energy of activation and of the pre-exponential factor observed upon changing the solvent, may be explained by the fact that the transition state close to the final is strongly polar, dissolves poorly in non-polar benzene and dissolves better in more polar alcohol. Correspondingly, the entropy of the transition state decreases significantly in benzene as a solvent.

The activation energy and the entropy of the transition state are very well described by the following equation:

$$\Delta S^* = 41.468 \times 10^{-4} \Delta H^* - 98.976$$

the constants for which were calculated according to the method of least squares. This is illustrated by Table 2.

Table 2

Activation energy	$-\Delta S^{\neq}$	$-\Delta S^{\neq}_{\text{calcul.}}$
17 400	27.03	26.82
16 480	30.59	30.64
15 080	36.15	36.44
13 120	44.60	44.57
11 400	51.80	51.70

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GEOCHEMISTRY

CONTRIBUTION TO OUR KNOWLEDGE OF THE MAIN PHYSICO-CHEMICAL MECHANISMS GOVERNING THE DEVELOPMENT OF SALINE LAKES

By M. G. VALIASHKO

(Communicated by W. I. Vernadsky, Member of the Academy, 8. III. 1939)

I. SUBDIVISION OF LAKES ACCORDING TO THE CONCENTRATION OF THE SOLUTION IN THEM

The study of salt lakes, as one of the phases in the migration of natural waters and of the salts dissolved therein through the earth's crust, presents quite outstanding scientific and practical interest.

By the present moment we possess already substantial data regarding the main lacustrine regions of the USSR (the Kulundinsky steppe, the Crimea, the Kalmuck region, the Ural-Emba territory), while a yet greater number of lake regions are still under investigation (Middle Asia, Kazakhstan, Eastern Siberia).

Numerous expeditions sent annually to salt lakes located in most different parts of the Soviet Union and special investigations devoted to their study are accumulating every year a wealth of factural evidence and are opening up always new and new sources of natural riches.

Possibilities are thus fully available and the need is ripe for drawing generalized conclusions out of the material gathered. In the present series of works an attempt is being made on the basis of available experience to ascertain the basic processes involved in and to bring to light certain fundamental mechanisms associated with the development of salt lakes.

According to modern views, a salt lake is a very complex aqueous system, highly mobile chemically, the general trend of processes in which (displacement of equilibrium) depends upon the physico-chemical nature and the properties of the components (salts) which form the bulk of the lake solution. Other important factors involved are: the concentration of the solution and the surrounding conditions connected with the geological and geographical location of the lake (the materials of which the bottom of the lake is made up, nature of adjacent rocks and soils, run-off, climate, etc.).

Changes in these conditions are apt to impair the equilibrium of the solution and to bring about a tendency towards a new form of equilibrium which would be stable under the given new conditions. In other words, changes in external conditions call forth processes which continuously, though in a different measure, tend to change the composition of the solution of the lake.

Thus, the prime object of the study of salt lakes consists in finding the mechanisms governing the changes in the composition of the lake solution depending upon changes in external conditions ([1], [2]).

The present investigation is based on a close connexion between composition and condition viewed not as stationary state, but as being in perpetual development.

The salts entering the brine of lakes are very numerous and, possibly, it is even difficult to take them into account exactly. For the physical chemist, who considers a lake as a system in equilibrium, the prime object consists in segregating from all the salts that are dissolved in the brine of a lake that very minimum quantity of components which would characterize the lake from a physico-chemical point of view and would thus permit of giving a theoretical foundation to a detailed study. This had best of all been accomplished by laboratory work which would involve a detailed study of the properties of the system formed by the given salts (we may consider as the most important property—the joint solubility of salts at different temperature).

The impossibility of studying such an equilibrium system for each separate lake requires, with a view to making the investigation the most fruitful, to bring out several basic types which would, on the one hand, permit of summing up all the multiplicity of the compositions of lake solutions, reducing them to certain basic chemical types with a minimum number of components, and on the other hand, would permit of determining and expressing in the simplest possible reactions the mutual connexions of these types. However, prior to passing to the solution of this basic problem it is necessary to dwell at some length on the concentration conditions which would permit of considering a lake as a salt lake.

The waters of lakes are a variety of natural waters which W. I. Vernadsky divides according to concentration into three main classes. He suggests the following classification ([3], [4]).

1. Fresh water lakes, containing mineral matter up to 0.1% by weight
2. Salt » » » » » from 0.1 to 5.0% by weight
3. Brine » » » » » » 5% by weight and up

By mineral components we must understand the molecules of all substances other than water which are dissolved in H_2O. Dissolved gases are not included. From a practical view point we may consider the mineral portion to be the dry residue after the evaporation of water.

The boundary for concentration in fresh water lakes stated at 0.1% by weight is not a casual or arbitrary figure and is close to the limit, below which natural fresh water life is apt to develop in non-salinized aquatic bodies, this life being well known to differ sharply from the fauna and flora of salt water bodies. As regards the demarcation line separating salt and brine waters, W. I. Vernadsky considers it to be conventional, though he does state that above this concentration hydrated complexes instead of the ions prevailing below the demarcation line are predominant in the aqueous solution.

While making good use of the principles of this classification for subdividing lakes on the basis of the concentration of their waters, the writer deems it necessary to introduce the following amendments into W. I. Vernadsky's scheme.

1. The concentration boundary separating salt lakes and brine lakes had better be lowered to 3.5% by weight. This appears to be more convenient, since very many salt lakes are genetically (directly or indirectly) connected with oceans and seas, the concentration of water in which, as it seems to us, can very well be selected as the criterion for distinguishing lakes with salt and brine waters ([1]).

2. For lakes with a concentration of water exceeding 3.5% by weight the author suggests the use of a new term, namely, that of s a l i n e lakes,

instead of the frequently used term brine lakes, or s a l t lakes. It would seem that the new term would be more conformable to the essence of the matter and would, moreover, be apt to exclude the personal judgment in evaluating this or other lake.

3. We should suggest calling the intermediate group of lakes with waters mineralized within 0.1 to 3.5% s a l i n i z e d lakes, this being advisable in order to avoid any ambiguity due to the practice of frequently designating (both in literature and practice) by the term «salt» such lakes, in which the concentration of brines by far exceeds 3.5%.

Thus, we obtain the following scheme for subdividing lakes on the basis of the concentration of water in them.

1. Fresh water lakes with a concentration of the solution up to 0.1% by weight
2. Salinized » » » » » » » from 0.1 to 3.5% by weight
3. Saline » » » » » » » » 3.5% by weight and up

All our further considerations of the problem concern only saline lakes, i. e. lakes having a concentration of their solution exceeding 3.5% by weight and existing under the conditions of the surface of the earth*.

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II. AN ATTEMPT AT DRAWING A NATURAL CLASSIFICATION OF SALINE LAKES ACCORDING TO THE CHEMICAL COMPOSITION OF THEIR BRINE

On the basis of the considerations outlined in communication I ([1,2]) let us make an attempt to deduce the main chemical types of natural lake-brines from the physico-chemical properties of the solutions formed by the components of natural waters.

For this purpose let us consider in first place the composition of the saline mass of a lake solution which we shall express in terms of ions, binding them up, as need arises, into salts in conformity with accepted practice, i. e. according to the solubility diagram (in the order of their segregation).

The ions which occur in appreciable quantities in the brines of salt lakes are as follows:

Cations: Na^+, Mg^{++}, Ca^{++} (K^+)
(K^+), Li^+, Rb^+, Cs^+, NH_4^+, Ba^{++}, Sr^{++}, Al^{+++}, Fe^{++}, Fe^{+++} etc.
Anions: CO_3'', HCO_3', SO_4'', Cl'
Br', I', HS', B_4O_7'', PO_4''', NO_2', NO_3', SO_3'', OH', SiO_3'' etc.

Both anions and cations can be subdivided into two categories: 1) The m a i n ones (the upper line in every group) and 2) the s e c o n d a r y ones (the lower line). Under the head of „main" we consider those ions, whose quantity is considerable and whose availability is either constant or defini-

* For such lakes which by their origin, feed, etc., are connected with an extant sea, the concentration in which is below that of the ocean (e. g. the Black Sea, where it is 2.0%), we must take for this boundary the concentration of the particular sea with which the lake is connected. For littoral lakes this boundary will to a certain extent depend on the location and the genesis of the lake in question.

tely characteristic for the type of lake in question as determining its physico-chemical features; „secondary" ions are generally met with in very small quantities and their presence fails to be constant.

From the above-mentioned list it is readily seen that Na^+, Mg^{++}, Ca^{++} belong to the class of the „main" ions, while K^+ is under doubt. This element being in respect of its chemical properties a counterpart of sodium and occurring frequently in saline lakes in rather considerable quantities should, as it appears, be considered under the class of main cations. However, certain peculiarities connected with reaction to it of living matter and colloids capable of rapidly throwing it out of solution, permit of classing it under this head not without qualification. All other cations belong to category II.

From among anions CO_3'', HCO_3'', SO_4'' and Cl' will fall under the head of the main ones. We might perhaps also class under the same head Br', B_4O_7'', but owing to the very small amounts in which these anions occur in brines we, nevertheless, consider them as belonging to group II. All the other anions written out in the second line belong definitely to the second category.

In the subsequent, in drawing our conclusions regarding the various types of saline lakes, we shall confine ourselves only to the «main» ions, namely to those of the first category, without taking the second group at all into account, even though some ions from this group, namely K^+, Br', B_4O_7'', have very great practical significance.

We are thus in a position to consider the brine of a saline lake as a certain combination of the above-mentioned seven or eight ions of the first category in aqueous solution.

Numerous investigations connected with solubility of water systems containing these ions, carried out by a number of authors, enable us to give not only a qualitative, but also a quantitative characteristic.

Let us consider the possible combinations of the above-mentioned anions and cations in an aqueous solution, on the basis of the physico-chemical properties of the respective system, that is assuming anions to be independent and cations dependent variables.

Case I. All four anions CO_3'', HCO_3', SO_4'' and Cl' are present in the solution; from among cations Na^+ (K^+) may be in solution, and only traces of Mg^{++} and Ca^{++}.

Case II. From among anions CO_3'' and HCO_3' * are absent, SO_4'' and Cl' are present; from among cations Na^+ (K^+), Mg^{++} and small quantities of Ca^{++} may then be present (in more concentrated solutions they are practically non-identifiable).

Case III. From among anions are absent: CO_3'', HCO_3', SO_4'', only Cl' is present. From among cations, all may then be available, i. e. Na^+, (K^+), Mg^{++}, Ca^{++}.

In conformity with the three types considered, we may subdivide the brines of salt lakes on the basis of their chemical composition into the following three categories: 1) the carbonate type; 2) the sulphate type; 3) the chloride type.

Each of these types of brines may be characterized by its salt composition [in analogy with that introduced by N. S. Kurnakov(3)].

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* It would seem more relevant to exclude only CO_3'' leaving HCO_3', yet obtaining such solutions under laboratory conditions involves a definite procedure, while under natural conditions the same set of conditions is highly improbable.

Let us now consider in detail each of the three types of brines:

1. Carbonate Type

a) Salts available:

Na_2CO_3,	$NaHCO_3$,	Na_2SO_4,	KCl
$MgCO_3$ } traces	—	—	—
$CaCO_3$ }	—	—	—

b) Coefficient characteristic of the condition of the lake:

$$K_I = \frac{\text{Sum of carbonate alkalis}}{Na_2SO_4} = \frac{Na_2(K_2)\,CO_3 + Na\,(K)\,HCO_3}{Na_2SO_4}$$

2. Sulphate Type

a) Salts available:

NaCl,	Na_2SO_4,	—	
$MgCl_2$,	$MgSO_4$,	$Mg(HCO_3)_2$	} traces
—	$CaSO_4$	$.\,Ca(HCO_3)_2$	}

b) Coefficients characteristic of the condition of the lake:

$$K_I = \frac{Na_2SO_4}{MgSO_4};\quad K_{II} = \frac{MgSO_4}{MgCl_2}$$

3. Chloride Type

a) Salts available:

NaCl,	—	—	
$MgCl_2$,	—	$Mg(HCO_3)_2$	} traces
$CaCl_2$,	$CaSO_4$	$,Ca(HCO_3)_2$	}

b) Coefficient characteristic of the condition of the lake:

$$K_{III} = \frac{MgCl_2}{CaCl_2}$$

The coefficients indicative of the lake belonging to this or other type which we, following N. S. Kurnakov ([3], [4]), shall hereinafter call the coefficients of metamorphization, will vary from one type of brine to another in the following way:

	$K_I = \frac{\sum \text{carb. alk.}}{Na_2SO_4}$	$K'_{II} = \frac{Na_2SO_4}{MgSO_4}$	$K''_{II} = \frac{MgSO_4}{MgCl_2}$	$K_{III} = \frac{MgCl_2}{CaCl_2}$
Carbonate type . .	n	∞	—	—
Sulphate type I	0	n	∞	—
Sulphate type II	—	0	n	∞
Chloride type . .	—	—	0	n

Although in natural brines, and sulphate and chloride concentrations, traces of the anions CO_3'' and HCO_3' are always available, while in a chloride concentration SO_4'' is also to be found, yet, their influence is so small that it fails to have any effect upon the distinguishing physico-chemical features of the lake. For the carbonate type the main equilibrium system characteristic for the physico-chemical processes in the lake is as follows:

$$Na_2CO_3 - NaHCO_3 - Na_2SO_4 - NaCl - H_2O$$

K^+ and B_4O_7'' may also be added here.

For the sulphate type the main system is as follows:

$$2NaCl + MgSO_4 \rightleftarrows Na_2SO_4 + MgCl_2.$$

For the sake of completeness we can add here also K^+ and Ca^+.

For the chloride type the basic system will be as follows:

$$NaCl - MgCl_2 - CaCl_2 - H_2O - (KCl).$$

A study of the basic properties and the construction of chemical diagrams of these equilibrium systems provides us with possibilities for understanding the basic physico-chemical processes occurring in the lake. A check of the suggested classification through a large number of analyses taken from the brines of saline lakes with most different genesis, geographical location and geological occurrence shows that the three simplest chemical types of brines suggested by us cover all the variety of compositions of saline lakes throughout the globe*.

Comparing the classification of saline lakes suggested by us with other existing ones, we clearly see that our classification is virtually but a development of the first genetic classification of saline lakes proposed by N. S.Kurnakov ([3],[4]) who divided saline lakes into two genetically connected classes corresponding to our sulphate and chloride types. To this we add one more type—the carbonate type—and thus by filling a substantial gap we make the classification universal. In this connexion it should be said that the carbonate type of brine stands in the same genetical relation to the sulphate type (which corresponds to the first class in N. S. Kurnakov's classification) as the suphate type stands with reference to the chloride type (the second class of N. S. Kurnakov) which for the latter case has been ascertained by N. S. Kurnakov and then confirmed by a number of investigators. But this connexion, as will be seen from the subsequent, is more mobile and the general trend of the metamorphization process depends on the physico-geographical and chemical conditions for the given lake.

Schematically this connexion may be represented as follows:

$$\underset{\text{type}}{\text{Carbonate}} \rightarrow \underset{\text{type}}{\text{Sulphate}} \rightarrow \underset{\text{type}}{\text{Chloride}}$$

The arrows running from left to right show the direction of the normal course of metamorphization (metamorphization of the first kind), while the arrows running from right to left show the reverse course (metamophization of the second kind).

Our further communications will be devoted to a detailed analysis of the mutual connexion of these three basic kinds of brines.

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* The group of so-called acid lakes, i. e. lakes containing free sulphuric and hydrochloric acid in solution, which acids in certain cases reach a very high concentration (e. g. Green Lake), fails to fall within our classification. But these lakes call for quite specific conditions for their existence and cannot be considered as stable water bodies.

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HYDROCHEMISTRY

AGE OF THE RECENT LACUSTRINE PERIOD OF THE CASPIAN SEA AND METAMORPHIZATION OF SALTS OF THE RIVER DISCHARGE IN THE SEA

By S. W. BRUJEWICZ

(Communicated by W. I. Vernadsky, Member of the Academy, 9. IV. 1939)

Owing to its closeness and relative shortness of its last lacustrine period, as well as to the possibility of recording the salts carried in by the river discharge, the Caspian Sea offers better possibilities than any other sea for the study of the metamorphization of river salts after their entering the sea. Such a study is intimately connected with the determination of the age of the recent lacustrine Caspian Sea, i. e. of the period elapsed since its last union with the Azov-Black Sea basin.

A comparison of the salt composition of the recent river discharge into the Caspian Sea with that of the Caspian and oceanic shows that in respect to the main components the Caspian Sea occupies an intermediate position between the river discharge and the sea.

Thus, one may assume, in conformity with the geological history of the Caspian, that the recent Caspian waters could be formed as a result of changes in the oceanic waters or waters with a similar composition, under the action of the river discharge, as it was supposed by Lebedinzev ([6]). Knowing the total amount of salts in the Caspian and in the yearly river discharge, we can calculate how many years ago the ratio of two selected ions was the same as in oceanic waters. In case of a close agreement of «ages» determined according to different ions, we may assume safely enough that n years ago the salt composition of Caspian waters was practically identical with or almost similar to the composition of oceanic waters. In 1937 we made such a computation ([4], p. 43), using $Cl/Na+K$, Cl/Mg and Cl/SO_4 and obtained 6400, 10 600 and 10 600 years respectively. The first ratio and value are but little reliable, since the determination of alkali content of the river discharge lacks accuracy. Calculations after Cl/Mg were based on the assumption that the Ca of the river discharge passes entirely into the bottom deposits in the form of $CaCO_3$, while the whole of Mg remains in the solution. However, analyses of the bottom deposits of the Caspian showed that besides $CaCO_3$ these deposits contain also a certain amount of $MgCO_3$.

This permits of a recalculation of the age of the Caspian basing on the following assumptions: 1) the age calculated from Ca must evidently equal that calculated from Mg; 2) the total carbonate ion of the river discharge is fully precipitated in the form of $CaCO_3$ and $MgCO_3$.

Let us designate by (Cl) the total content of chlorine ions in the whole Caspian; by (Cl)′—the total amount of chlorine in the yearly discharge into

the Caspian; by (Ca)—the total content of Ca in the whole Caspian; by (Ca)′—the part of Ca in the yearly river discharge which remains in the sea; by (Ca)″—the part of Ca in the river discharge passing into bottom precipitates; by (Mg), (Mg)′ and (Mg)″—respective values for Mg; by K_{Ca} and K_{Mg}—the relation between the chlorine content and the ion in oceanic waters; and by n—the «age» of the recent Caspian. Thus, we obtain the following equations:

$$n = \frac{(Ca) \cdot K_{Ca} - (Cl.)}{(Ca)' \cdot K_{Ca} - (Cl)'} = \frac{(Mg) \cdot K_{Mg} - (Cl)}{(Mg)' \cdot K_{Mg} - (Cl)'};$$

$(Ca)' + (Ca)'' = 1.66 \cdot 10^7$ t (total amount of Ca in the river discharge during a year)
$(Mg)' + (Mg)'' = 3.18 \cdot 10^6$ t (total amount of Mg in the river discharge during a year)
$(Ca)'' \cdot 1.5 + (Mg)'' \cdot 2.47 = 2.44 \cdot 10^7$ t CO_3 (total amount of CO_3 in the river discharge during a year)

where $1.50 = \frac{CO_3}{Ca}$; $2.47 = \frac{CO_3}{Mg}$; $K_{Ca} = 46.1$ and $K_{Mg} = 14.84$

The solution of this system of equations gives a duration of 13 700 years for the last lacustrine period of the Caspian. This value, though considerably exceeding the age of the recent Caspian (10 600 years) previously calculated according to the ratio Cl/SO_4, is nevertheless a good approximation considering the unreliability of our knowledge of the river discharge and of its changes during the existence of the recent Caspian. We can tentatively accept an age of 13 000 years as an averaged value obtained from the ratios Cl/Ca, Cl/Mg and Cl/SO_4.

A value of the same order (9234 years) was obtained by Klochko [5] from Cl and SO_4. This author had at his disposal somewhat different figures of the chemical composition of the river discharge and Caspian waters*.

The above equations give not only the age of the Caspian, but also the amounts of Ca and Mg in the river discharge, precipitated in the form of carbonates and retained in the sea waters in solution.

Ca of the river discharge,	remaining in the sea $(Ca)'$ . . .	$= 1.5 \cdot 10^6$ t =	9%
» » » »	passing into precipitates $(Ca)''$.	$= 1.51 \cdot 10^7$ t =	91%
	Total . . .	$1.66 \cdot 10^7$ t =	100%
Mg » » » »	remaining in the sea $(Mg)'$ . . .	$= 2.5 \cdot 10^6$ t =	79%
» » » »	passing into precipitates $(Mg)''$.	$= 6.8 \cdot 10^5$ t =	21%
	Total . .	$= 3.18 \cdot 10^6$ t =	100%

From the total amount of carbonates contained in the yearly river discharge $2.44 \cdot 10^7$ tons of CO_3—$2.27 \cdot 10^7$ tons of CO_3 or 93% pass into deposits forming $3.78 \cdot 10^7$ tons of $CaCO_3$, and the remaining $1.67 \cdot 10^6$ tons or 7% pass into precipitates forming $2.35 \cdot 10^6$ tons of $MgCO_3$. According to theoretical calculations, the relation between $MgCO_3$ and the sum of carbonates in the bottom deposits is 0.059, or ~ 0.06.

The average value for this ratio obtained by analyses of the carbonate deposits of the southern Caspian, taking into account the deposits of the sea bed, amounts to 0.10. However, as the precipitation of carbonates takes place mostly at small and moderate depths and only to a very small degree

* We calculated the yearly river discharge into the Caspian assuming a composition identical with that of the Volga discharge which makes up 81.4% of the total discharge [for details see[1], p. 46]. It should be mentioned here that the computations of Klochko regarding the volume of the ancient Caspian waters are founded on a misunderstanding—the hydrochemical method offers no possibilities to calculate the volume of the ancient Caspian waters which certainly was not 4 times less than the recent, but, on the contrary, much higher. The value obtained by Klochko represents the volume of oceanic waters equivalent to that of the ancient Caspian by the content of chlorine and sulphate.

over the sea bed, the real relation of $MgCO_3/MgCO_3+CaCO_3$ must be near the mean arithmetical value (as yet the only one accessible to calculations) of the relation between shallow and moderately deep regions, i. e. 0.08. But actually the ratio of $MgCO_3/MgCO_3+CaCO_3$ in the deposits must be even lower, owing to the enormous distribution of mussels which did not enter into the samples analyzed and whose content of $MgCO_3$ is much lower.

The close agreement of age values calculated according to different pairs of ions, as well as of the theoretically computed and real ratio of $MgCO_3/MgCO_3+CaCO_3$ in sea deposits makes us confident of the correctness of the figures obtained; moreover, it testifies to that ca. 13 000 years ago the salt composition of Caspian waters was very close to that of the ocean. Consequently, there should have existed a connexion with the Azov-Black Sea basin which in its turn was connected with the Mediterranean Sea. Closely agreeing values are also obtained from calculations based only on the ratio $MgCO_3/MgCO_3+CaCO_3$ found in the Caspian deposits $=0.08$ (exceeding the real one). In this case the age obtained according to Cl/Ca amounts to 10 600 years and according to Cl/Mg to 15 500 years, the average being 13 000 years (when the ratio $MgCO_3/MgCO_3+CaCO_3$ decreases, the age values draw together; the ratio being 0.06, both values equal 13 700 years).

The value of 13 000 years obtained by us for the period elapsed since the time when the Caspian waters had a salt content approaching to that of the oceanic, corresponds according to the majority of geological data to the end of Wurmian freezing and, consequently, to the Khvalynskian transgression of the Caspian Sea (Borissiak). In particular this value is near to the time of the disappearance of the glacial sheet in the region of the Baltic Sea, as determined by De-Geer on the basis of varved clays (16 500 years).

The nearly oceanic composition of Caspian waters at that period may most naturally be explained by a water interchange between the Caspian and the Azov-Black Sea basins at the end of the Pleistocene. Here we may quote the ideas recently developed by biologists on the origin of the arctic species of the Caspian and, partly, of the Black Sea which have surely been carried in during the Quaternary. According to Högbom and Berg ([3]) this was due to the formation of glacial dammed lakes in the watershed of the Volga and northern rivers.

According to another view ([7]), the union of the basins took place at the beginning of the Quaternary at the period of maximum transgressions, when the Taimyr glacier cut off the Yenissey bay of the Kara Sea and raised the level of the Siberian rivers directing their discharge to the SW through Western Siberian into the Aral-Caspian depression. This variant, though accounting for the transport of arctic forms into the Caspian Sea, fails to explain the origin of the oceanic salt composition of the Caspian waters.

There is no unanimity in the opinions of geologists concerning the time of the last union of the Caspian and Azov-Black Sea basins. Archangelsky, Shatsky and oth.([1]) suggest the possibility of a discharge of the Caspian Sea into the Black Sea through the Manych river in the Khvalynsk time. However, it should be noted that Archangelsky refers the Khvalynsk transgression to the Riss-Wurmian interglacial epoch, and not to the post-Wurmian time (Borissiak and others). Pravoslavlev, pointing to that the deposits containing *Cardium edule* distributed on the Kumo-Manych lowland overlap the deposits of the Khvalynsk transgression, is inclined to refer the latest union of the basins to one of the last shiftings of the Wurmian ice ([4]). We are of the opinion that the ancient Caspian waters metamorphized by the action of the river discharge could be brought to a composition approaching that of the oceanic waters only during the period of a sufficiently intensive water interchange between the Caspian and the Azov-Black Sea basins. This,

in its turn, was possible only during an intensive retreat of the glacial sheet and an abundant discharge of thaw waters which raised the Caspian level to the level of the Black Sea. The salt composition of this lake-sea with flowing waters must have been near to the oceanic one (though probably not identical) as it is the case now in the Baltic, Azov and Black Seas. Taking into account the salt supply and the volume of the sea, the salinity could not have exceeded 6—7‰. Such a powerful water discharge was possible only at the period of the Caspian transgression, during the retreat of the Wurmian ice-sheet. The close agreement between ages calculated hydrochemically and those obtained by geologists points to the fact that the value and composition of the river discharge into the Caspian Sea during the Pleistocene were not subject to great changes.

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BIOCHEMISTRY

AMMONIUM AND NITRATE SUPPLIES COMPARED WITH REGARD TO THEIR EFFECT ON BIOCHEMICAL PROCESSES IN THE LEAVES OF *NICOTIANA RUSTICA*

By A. V. VLADIMIROV

(Communicated by D. N. Prianishnikov, Member of the Academy, 8. IV. 1939)

From his comparative study of the ammonium and of the nitrate form as sources of nitrogen supply for higher plants D. N. Prianishnikov has come to the statement ([1], [4]) that the former is physiologically the better form, since it is more readily converted into organic compounds than are the nitrates. According to Prianishnikov whose scheme of the conversion of nitrogen compounds in the plant is now generally accepted, the nitrates are reduced to ammonium by way of nitrates and other intermediate combinations, to serve as material for the synthesis of amides, aminoacids and proteins ([2], [3]).

Starting from that scheme we have supposed that inasmuch as the nitrate nitrogen is an oxidized form, it should on its reduction to ammonium oxidize other organic compounds, especially sugars, available in the plant organism and convert them into organic acids. On the other hand, the ammonium form, as a reduced form of nitrogen, cannot possibly provoke oxidation processes, but to the contrary is apt to set up reduction and thus cause the plant to store up organic acids in lesser amounts than it does under the influence of the nitrate form.

However, the metabolism of organic acids in plants in general and with reference to their mineral nutrition in particular has not been sufficiently investigated and therefore we have deemed it wise to perform some experiments on the influence of the nitrate and the ammonium form of nitrogen upon the metabolism of proteins, carbohydrates and organic acids in a plant, which work we have done in 1938 on the basis of the hypothesis mentioned above. As experimental plant we have chosen *Nicotiana rustica* because it is a valuable row material for the production of citric and malic acids. The experiment was conducted under condition of sand flowing culture solution in four series. Tap water was used in the preparation of all of the culture solutions. The latter had the following composition:

1) N 10 or 40 mg per litre, according to the plan of the experiment. In the nitrate series the plants were given a mixture of equal amounts of $Ca(NO_3)_2$ and $NaNO_3$, while in the ammonium series the equality between $CaNO_3$ and $NaNO_3$ was attained by adding respective amounts of $CaCl_2$ and Na_2SO_4 to $(NH_4)_2SO_4$.

2) P_2O_5—as KH_2PO_4, 1/5 of its dose in Hellriegel's medium.

3) K_2O—as KCl, 20 or 80 mg per litre according to the plan of the experiment.

4) The solution was adjusted to the requisite value of pH by adding $2n$ sulphuric acid. In view of the fact that ammonium sulphate is physiologically acid while sodium and calcium nitrates are alkaline, the solution in ammonium series was made to a less acid reaction than was that in nitrate series.

From the outset of budding 10 leaves were left on the experimental plants and further on all buds were continually being removed. The plants were harvested August 25 from 9 to 10 o'clock in the morning. Only blades of the 10 leaves were involved in the analysis, but the petioles with the main vein were cut off. Each leaf was halved along its mid-rib and one of the halves was kept in ether vapour for 30 min. and dried in a thermostat at 45—60° C, while another with the respective halves of the series was strung on a thread to undergo drying without conservation in ether in the shade of a greenhouse, as is generally used in the practice of tobacco culture. The analytical data reported here relate only to ether treated material.

The plan of the experiment and the data on yield are referred to in Table 1.

Table 1

Exper. series (concentr. of N and K_2O in mg/l)		Average leaf weight per plant in g	Average weight of a stem in g	pH of in-flowing solution
N	K_2O			
		NH_4 series		
40	20	156.0	42.7	6.0
10	20	151.0	46.7	6.0
40	80	161.8	33.3	6.0
		NO_3 series		
40	20	194.0	51.0	5.1
10	20	128.2	39.3	5.1
40	80	203.4	76.2	5.1

It is evident from the table that in the ammonium series the yield of leaf is greater compared to that in the nitrate series.

While studying how the biochemical processes which determine the amount and the quality of the yield are affected by the change in the concentration of ammonium and of nitrate nitrogen in the culture solution, we have analyzed the leaves for reduced and total sugars, protein and soluble nitrogen, nicotine, total acids and citric acid.

The data on chemical composition of the leaves of *Nicotiana rustica* are brought together in Table 2 against either of the nitrogen forms studied (in % of the weight of an air dry sample).

Table 2

Exper. series (N in mg/l)	Reduced sugars	Total of soluble sugars	Total acids in m-equ. per 100 g	Citric acid	Protein N, %	Soluble N, %	Nicotine, %
NH_4 (40)	0.33	0.46	141.2	0.55	2.52	3.15	7.56
NO_3 (40)	0.46	0.95	270.9	3.24	3.12	3.06	1.63

Following conclusions may be drawn from the data on the chemical composition of leaves.

1. Ammonium nitrogen used by the plant as nutrient gives rise to reduction processes inside the plant, and the latter shows, therefore, a sharply decreased content of total acids and citric acid.

2. Contrary to the plants of ammonium series the plants with nitrate nitrogen in the culture solution have their content of total acids and citric acid in the leaves greatly increased owing to the oxidation processes.

3. The content of nicotine is by far greater in the ammonium than in the nitrate plants.

We thus find the biochemical processes in the plant (and its metabolism of organic acids) to proceed in varying direction according to the form of nitrogen it is supplied with. The effect of the concentration of ammonium and of nitrate form in the culture solution upon the chemical composition of leaves in *Nicotiana rustica* is brought out by the data in Table 3 (in % of the weight of an air dry sample).

Table 3

Exper. series (N in mg/l)	Reduced sugars	Total soluble sugars	Total acids in m-equ. per 100 g	Citric acid	Protein N, %	Soluble N, %	Nicotine, %
NH_4 (40)	0.33	0.46	141.2	0.55	2.52	3.15	7.56
NH_4 (10)	0.77	2.15	181.7	1.15	2.25	3.16	7.96
NO_3 (40)	0.46	0.95	270.9	3.24	3.12	3.06	1.63
NO_3 (10)	3.87	5.45	259.3	1.22	2.13	2.10	0.87

The evidence furnished by these data is that:

1. The increase in the concentration of the ammonium as well as of the nitrate form of nitrogen in the culture solution from 10 to 40 mg per litre results in a sharp decrease in the content of reduced and total soluble sugars in the leaves of the plant.

2. Concomitant with the decrease in sugars due to enhanced concentration of nitrogen is the increase in total and protein nitrogen as well as in nicotine, which fact should be taken to mean that sugars are used by the plant in the synthesis of nitrogenous organic compounds.

3. The ratio of total acids and that of citric acid go down as the concentration of ammonium nitrogen goes up, whereas in the case of nitrate nitrogen the increase of concentration makes both of these ratios rise sharply.

The fact that the biochemical processes, especially the metabolism of organic acids, in the plant are differently directed by the ammonium than by the nitrate form of nitrogen, may easily be interpreted in terms of our concept. While nitrate nitrogen as an oxidized form set up conditions for the oxidation processes to prevail, reduction was favoured by the ammonium form. The result of enhanced oxidation was the increased content of total organic acids in general and citric acid in particular. On the other hand, reduction resulted in a sharp decrease in both total acids and citric acid.

The effect of varying concentration of potassium in the culture solution was also followed up in the experiment. The data in Table 4 show how this factor tells upon the chemical composition of leaves in *Nicotiana rustica*.

Table 4

Exper. series (N and K_2O in mg per litre)	Reduced sugars	Total soluble sugars	Total organic acids in m-equ. per 100 g	Citric acid	Protein N, %	Soluble N, %	Nicotine, %
NH_4 (40)+K_2O (20) .	0.33	0.46	141.2	0.55	2.52	3.15	7.56
NH_4 (40)+K_2O (80) .	0.59	0.59	—	0.34	2.54	4.10	7.54
NO_3 (40)+K_2O (20) .	0.46	0.95	270.9	3.24	3.11	3.06	1.62
NO_3 (40(+K_2O (80) .	0.43	0.88	208.3	2.20	1.81	2.82	1.03

From these data it may be seen that the effect of increased concentration of potassium in the culture solution is to decrease the content of sugars in the leaves of *Nicotiana rustica* which becomes simultaneously lower in both total acids and citric acid.

We have thus disclosed by experiment that the biochemical processes, say the metabolism of organic acids, in the leaves of *Nicotiana rustica* vary in direction according to the conditions of nitrogen and potassium supply ([6]). This fact must be taken into account to make the use of various forms of nitrogen fertilizers consistent with the economic purpose of *Nicotiana rustica*.

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HYDROBIOLOGY

COEFFICIENTS OF DIURNAL VERTICAL DISTRIBUTION OF PLANKTON

By B. G. BOGOROV

(Communicated by S. A. Zernov, Member of the Academy, 10. IV. 1939)

It is well known long since that the vertical distribution of plankton is subject to considerable daily variation. Most of the animals at day-time desert the superficial layers to accumulate there at night in huge quantities. On the contrary, as shown by Hardy's observations (3), the alga *Coscinodiscus* ascends at day-time to the surface and sinks at night to a depth of 50 m. As these vertical shiftings occur regularly (daily), the water column involved can be regarded as the normal habitat of the migrating organisms. Consequently, all the hydrological conditions encountered in different water layers through which plankton is migrating, coincide with the characteristic ecological conditions of the organisms. Hence the methodical question—how to make comparable the vertical plankton distribution on stations taken at different hours?

One way is to take the samples always at the same time, having previously settled whether it is to be the «day-time» or the «night-time» vertical distribution.

Another solution consists in taking all the samples on daily stations only.

Each of these methods has its methodical and technical drawbacks. In the first case we obtain an artificially assorted material which gives no proper notion of the diversity of the plankton distribution and behaviour. Besides, the term of the cruise is artificially prolonged. In the second case, though everything seems to be all right, the term of the cruise is protracted to a degree which makes the comparison of the different parts of the work almost impossible. Moreover, this is not a feasible plan for an expedition to be based upon, since none of the investigations carried out during a complex expedition require such long halts. On the contrary, methodically there is often a need of «flash» surveys of the regime of the sea or of the distribution of fish. With such a system the plankton may become isolated from the complex of oceanographical and ichtyological investigations.

Thus, as a principal method of plankton sampling (not for specific purposes) must be adopted the usual expeditional work, envolving stations taken at fixed places when the ship arrives at the appointed place. All that is necessary is to devise a method which will permit of a quantitative and qualitative evaluation of the day-time and night-time vertical distribution both of different species and the bulk of the plankton.

For the determination of the general geographical distribution of the biomass of plankton in the sea we can use the method widely applied by V. A. Iashnov (5), consisting in the evaluation of the total quantity of organisms or plankton matter in a water column beneath a certain area of the sea.

Theoretically the number of organisms under a given area comprises all the organisms, irrespective of the variation of diurnal distribution (the only difficulty is the recording of plankton benthonic animals at day-time). However, this method fails to represent the vertical distribution of plankton organisms and their appurtenance to definite layers, either in general or at a given hour. It is impossible to determine the feeding value of different layers either (2).

The determination of the vertical distribution of plankton as well as of its geographical distribution must be based on the day-time and night-time distribution. It stands to reason that such a classing of the whole material into two groups—a light and a dark one—is also rather artificial and nevertheless the comparison of day-time or night-time distributions on different stations or over the general map of the biomass of plankton upon the whole area of the sea will be more reliable. The evaluation of the abundance or paucity in different water layers or sea regions will be almost independent of the time of work on the station.

Thus, to find out the vertical distribution of plankton as well as its distribution over the area (plankton map) we deem it necessary to give two pictures—one of the day-time distribution, and the other of the night-time distribution of the organisms, or the biomass of plankton.

Therefore we find it necessary to introduce special coefficients of the daily (24 hours) vertical plankton distribution (instead of the daily vertical migrations). With their help it will be possible knowing the time at which the work on the station was done, to reconstruct the picture of the diurnal, or nocturnal, or eventually, even of the hourly vertical distribution of organisms. Such coefficients of the daily vertical distribution of plankton are furnished by the percentage of a given organism during a 24 hours' period in all the water layers from bottom to surface.

Thus, for instance, as the result of treatment of one daily station in the Caspian Sea (9—10 December 1934, 39° and 52°06′) we obtained the following percentages of *Eurytemora grimmi* at different hours in different water layers from the surface to the bottom (Table 1).

Table 1

Water layers \ Time of catch	18	20	23—24	2	5	8	11	14	Day-time	Night-time
									coefficients	
10—0 m	20	30	30	20	5	1	1	1	2	25
25—10 »	50	60	50	60	20	—	—	39	15	55
50—25 »	30	9	18	18	70	11	1	30	28	19
85—50 »	—	1	2	2	5	88	98	30	55	1

Such percentages of the total quantity of organisms in the whole water column at a given hour can be used as coefficients of the daily vertical plankton distribution. Indeed, now we can easily calculate the distribution of *Eurytemora grimmi* within different layers at requisite hours, or day-time and night-time (the light and the dark hours of a 24-hour period), for any station taken at any time. For instance, if a station is taken at 14 hours and the total number of *Eurytemora grimmi* amounts to, say, 1000 individuals, at 18 hours there will be 20%, or 200 individuals in the layer 10—0 m, 500

individuals in the layer 25—10 m and 300 individuals in the layer 50—25 m. Expressing the number of organisms in weight units, we obtain the distribution of the biomass. Obviously, these data cannot be regarded as absolute figures, but they express the order of quantitative variation with a sufficient accuracy. Thus, in order to form an idea of the day-time and the night-time plankton distribution, we have to use the mean day-time or night-time coefficients.

We may also be confronted with the necessity to evaluate the eventual variations of the quantity of plankton within a 24-hour period in different layers not from a whole series of hauls from surface to bottom, but from separate hauls (samples) taken in one or a few layers only. It stands to reason that in such a case our task will be more complicated and the possibility of obtaining figures which reflect the actual quantitative variations is reduced. But even in this case it may be possible to introduce coefficients of the daily vertical distribution by layers. Such layer coefficients must be based on the percentage of a given organism in a given layer during a 24-hour period.

Thus, we obtain for *Eurytemora grimmi* on our station the following layer coefficients (Table 2).

Table 2

Time	18	20	23—24	2	5	8	11	14	%
Water layers									
10—0 m	16	28	29	24	1	1	1	1	100
25—10 »	19	20	16	21	7	1	1	15	100
50—25 »	15	3	8	11	36	7	1	20	100
85—50 »	1	1	1	1	2	40	43	12	100

The number of individuals in a given layer at a definite time being known, we can determine the daily quantitative variations with the help of these layer coefficients. Thus, for instance, if in the layer 10—0 m at 2 hours a. m. there are 100 organisms, we may assume that at 18 hours their number in the same layer will be 67 (16%); at 20 hours it will amount to 117 individuals (28%), at 23—24 hours to 121 individuals (29%) and at 5, 8, 11 and 14 hours to 4 individuals (1%). Of course, it is not the accuracy up to a unit of the figures obtained that matters, but the determination of the order of quantitative variations.

With the help of the coefficients of daily vertical distribution, the material collected at different hours can be made comparable. This insures a better understanding of the character of the vertical plankton distribution and of the ecology of different species. Moreover, it makes possible to draw a map of day-time and night-time plankton distribution and to estimate the food value for fishes of different water layers and sea regions at different hours of the day.

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HYDROBIOLOGY

SEX RATIO IN MARINE COPEPODS

(On the Problem of the Evaluation of Plankton Production)

By B. G. BOGOROV

(Communicated by S. A. Zernov, Member of the Academy, 10. III. 1939)

Investigations on the sex ratio in marine copepods, besides their general biological value, are of great interest in connexion with the study of plankton production. However, this problem is as yet insufficiently investigated. Separate data or notes concerning the sex ratio of marine copepods are found in the papers by Lücke (4), Otten (5), Tesh (7), Iashnov (9) and Bogorov (1), but the data of all these authors (with the exception of Bogorov) refer to adult forms only. Such a gap is due to the fact that up to recently the treatment of plankton failed to include records of all age stades for each sex separately.

In copepods sex differentiation usually takes place at the IV copepodite stage. Consequently, there is no difficulty to investigate the sex ratio of the IV and V stages and the adult forms.

The great difference in the numerical strength and frequency of males and females is a striking feature in plankton investigations which stands out even without special calculations. As a rule, female copepods are more numerous than males. In different species and individual samples (by seasons or regions) the number of females is often 10 and even 100-fold that of males. In some species (for instance, *Calanus finmarchicus*) the occurrence of males is a rarity during the major part of the year. A preponderance of males is observed but very seldom (Table 1).

Table 1

Ratio ♂ : ♀

Sea	North Sea			White Sea	Barentz Sea
According to data	Otten	Lücke	Tesh	Bogorov	Bogorov
Pseudocalanus elongatus	1 : 4.5	1 : 4.9	1 : 3.12	1 : 32	1 : 4
Metridia longa	—	—	—	1 : 1.3	1 . 1.1
Oithona similis	—	—	—	1 : 33	1 : 7
Harpacticus superflexus	—	—	—	1 : 5	—

A. V. Okul was kind enough to inform us (unpublished data on the Azov Sea plankton) that comparing the ratio of male and females copepods during a 8 month period of 1937 he observed a considerable prevalence of females.

Table 2 shows the number of months with predominances of one of the sexes.

Table 2

	♀ > ♂	♀ < ♂	♀ = ♂	Organisms are absent in
Paracartia laticetosa	5	1	1	December and February
Acartia clausi	7	—	1	—
Centropages kroyeri	3	1	3	February
Calanipeda aquaedulcis	3	4	—	October
Heterocope caspia	4	—	—	October, November, December and February

Consequently, only in *Calanipeda* we may observe respective prevalence of females or males during an almost equal period of time (in months).

Individual cases of prevalence of males were recorded by V. A. Iashnov for *Pseudocalanus elongatus* (♂ : ♀ =2 : 1) in the Kara Sea and by B. G. Bogorov for *Acartia longiremis* (♂ : ♀ =1 : 0.7) in the Barentz Sea. However, this is characteristic for certain stations only.

Disposing of a vast material from different polar seas (the collections of the cruise of the r/s Litke, 1934) we have determined the sex ratio for several species of copepods. Unfortunately, this question was not given special attention during the treatment of the material, so that (owing to lack of time) sex differences were recorded for adult individuals only, while but scattered data on the sex ratio of young are available.

Summing up all our data on the polar seas from the Kara to the Bering Sea and for *Paracalanus parvus* from the Norwegian coast, we obtain the following mean numerical ratios and frequencies of males and females (Table 3).

Table 3

	Ratio ♂ : ♀	Frequency % ♂	Frequency % ♀
Calanus finmarchicus	1 : 36	13	87
Pseudocalanus elongatus	1 : 12	34	66
Limnocalanus grimaldi	1 : 9	27	63
Drepanopus bungei	1 : 30	46	54
Paracalanus parvus	1 : 20	40	60
Oithona similis	1 : 5	50	50
Acartia longiremis	1 : 1.4	24	76
Acartia clausi	1 : 5	38	62

Thus, both the prevalence and higher frequency of females are obvious.

Separate data on other species also point, as a rule, to a higher proportion and frequency of females. Thus, for instance, on 5 stations we obtained usually twice as much females as males of *Temora longicornis*. There was also a greater number of adult females of *Metridia longa*. And only *Centropages typicus* showed almost equal proportions and numbers of males and females.

What is the cause of so universal a phenomenon of the quantitative prevalence of adult females in copepods? Two assumptions way be advanced. 1) Male copepods at younger stages of development are less viable compared with females, and consequently, show higher mortality up to the adult stage, 2) or else equal numbers of males and females survive till the adult stage after which adult males die at a far higher rate than females.

For a full comprehension of the sex ratio in young copepods more material is needed than we dispose of at present, but the character of this ratio is quite representative. Thus, according to our data for the Barentz and White Sea we obtain the following sex ratios for the young stages of *Pseudocalanus elongatus* and *Metridia longa* (Table 4).

Table 4

Copepod. stages	*Pseudocalanus elongatus*		*Metridia longa*
	Barentz Sea	White Sea	White Sea
IV	1 : 0.7	1 : 1.15	1 : 0.9
V	1 : 1.2	1 : 1.05	1 : 0.65

From the material collected by the Litke expedition we can use only the data concerning the V stage of *Pseudocalanus elongatus*.

On 10 stations were obtained the following numbers of males and females (on 1 m^3) (Table 5).

Table 5

♂	♀	♂	♀
200	200	—	7
40	30	7	2
—	10	2	4
—	10	12	9
4	—	5	10

Thus, there is no material prevalence of young females, but even a somewhat greater number of males.

Equal, or almost equal numbers and frequencies of young male and female copepods are a typical phenomenon, which strikes one when treating young stages (IV and V) even without separate counts for each sex.

Thus, we naturally pass to the second question. Indeed, there is an equal survival of males and females till the adult stage with a subsequent mass mortality of adult males, or rather there is a difference in the longevity of males and females. Males survive only for a short period, apparently not greatly exceeding the period of fertilization*, while females are living longer, during all the spawning period and afterwards. Thus, an almost equal number of males and females observed in the earlier stages of life is rapidly changed to an enormous prevalence of females in the adult forms. The more advanced is this process, the larger is the relative number of females observed. This accounts for the diversity in the sex ratio of adult copepods observed on stations taken at different seasons at different sea regions.

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* Besides these indirect data, we have also direct observations. Thus, Campbell [10] observed in *Euchaeta japonica* a rapid dying off of males after fertilization.

Hence arises another question: what becomes of the enormous biomass of plankton composed by a rapidly dying off mass of males? In adult copepods the biomass of males is at the beginning almost equal to that of the females, whereas later we have to deal chiefly with the biomass of females.

It is impossible to suppose a more intensive consumption (eating out) of male copepods as compared with female ones. We have only one indication ([6]) and that based only on two samples, according to which males of *Pseudocalanus elongatus* prevailed in the food of the herring fry in the Aberdeen region. However, these observations are not confirmed by the investigations of L. A. Chajanova (White Sea herring)([8]), G. V. Boldovsky (Murman herring) ([3]), A. V. Okul (Azov Sea anchovy a. oth.). To regard this as a general rule is quite incompatible with the biology of copepods and plankton eating fish. Moreover, as seen from the data of Ogilvie, a prevalence of males in the food was observed only for *Pseudocalanus* and was not confirmed for other species. It seems that the data of Ogilvie are the result of some local or temporary factors having no general importance.

Consequently, the major part of the huge plankton biomass consisting in adult males rapidly dying off disappears from the food chain of plankton-eating fishes (and, possibly, of others animals) and either dissolves and sinks down, or is consumed by bottom mud-eaters as decomposing corpses.

The study of this subject has a great importance for the determination of the value of plankton production. It should be noted that in general the phenomenon of the natural dying off of plankton is the least studied of the whole problem of productivity. It is time to give this phenomenon more attention.

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GENETICS

PHYSIOLOGICAL VARIATION WITHIN THE ENGLISH RACE-HORSES

By V. I. PATRUSHEV

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According to Charles Darwin's theory of selection, the differences among breeds result from selection for changes in body structure, rate of growth, productivity, etc. Hereditary departures from the mean type of the breed are mostly not great and, as pointed out by Ch. Darwin, often inconspicuous. The latter circumstance always created difficulties to breeders. We believe that hereditary variations in productivity of the animals are caused in the first place by changes in activities of the basic physiological systems of the organism. To work out a modern theory of breeding, we find it necessary to study differentiation among and within breeds in physiological and biochemical factors, as connected with the performance of the animals. Modern methods of clinical examination of animals make it possible to determine even slight deviations in the general and particular metabolism, the aim of the zootechnician being to establish the value of these deviations for animal breeding. The correlation between the physiological differences within breeds and productivity was convincingly demonstrated by a number of investigations.

It stands to reason that differences among breeds should be less pronounced and show stronger transgression of characters. The common statistical way of analysis of the differences (tripple error, etc.) are not always applicable here. In the majority of cases one may judge, in our opinion, of the probability of the differences by the similarity of the direction of variation in a series of groups of animals as well as by many other indices which characterize a common process from different sides.

In 1938 we have conducted a physiological investigation of the horses at the Moscow hippodrome. The results of the investigation show that animals of the same sex and age which attain larger sizes and higher body weight on the average show higher concentration of red blood, glutathione, serum proteins, as well as higher globulin content in the serum. In Table 1 are presented data on the relation of blood composition to body weight in one of the larger homogeneous group of horses.

The plus and minus variants in relative volume of the blood cells on the average differ in body weight by 10 kg. Among the plus variants in concentration of the red blood there appear, moreover, minus variants in other factors which are correlated with body weight, viz., glutathione, proteins, etc. Plus variants in two factors, for instance both in relative volume of the blood cells and dry substances, differ from the minus variants by 20 kg of the mean body weight. When four factors are considered, the difference in body weight

Table 1

Blood factors	± variants in blood composition	Body weight							
		in 1 factor		in 2 factors			in 4 factors		
		n	*M*	± variants	*n*	*M*	± variants	*n*	*M*
Relative volume of blood cells	+	25	445	+	17	451	+ +		
	—	24	435	+					
Dry substance	+	28	449	—	18	431	+ +	11	460
	—	25	432	—					
Total glutathione	+	23	450	+	21	452	— —		
	—	24	429.8	+					
Reduced glutathione	+	24	448	—	21	429.7	— —	14	429
	—	23	430	—					
Total protein of the serum (after Robertson)	+	14	442	+	8	438			
	—	13	434	+					
Per cent of globulins in the serum	+	14	438.7	—	5	417			
	—	13	437.6	—					

between plus and minus variants exceeds 30 kg. In other words, from the complex of physiological indices it is possible to establish within a breed individual deviations in activities of the basic systems of the organism, these deviations causing differences in the rate of growth and early maturation (or being at least correlated with them). The very fact of the existence of individual differences makes one hope that they will be manifested and augmented in the progeny in case necessary conditions are created and constant selection of suitable parents is practised.

Within a breed there is a differentiation in the type of constitution. In Table 2 are presented the averages for a number of blood factors in plus and minus variants in the index of eurosoma. Physiological differences between eurosomal and leptosomal animals are not great within a breed, though relatively stable. In all the groups of leptosomal animals compared there is a somewhat augmented concentration of red blood, whereas in eurosomal one there is an increased content of glutathione of the blood and of globulins of the serum. The latter fact shows that eurosomal animals, evedently, reach maturity somewhat earlier than leptosomal ones.

In Table 3 are presented physiological differences among distinct lines of English race-horses. Horses of the line Hetman are distinguished by the highest factors except those of glutathione and erythrocyte sedimentation. The differences between the lines of Brimston and Tagor are less expressed.

Within the limits of a breed of pure-bred English race-horses there are thus physiological-biochemical differences connected with differences in origin, type of constitution, growth and body size. 1) Animals of the same age possessing maximum factors of concentration of red blood serum proteins, content of serum globulin and concentration of glutathione of the blood are of larger size as compared to minus variants in the factors enumerated above. 2) Concentration of the total and reduced glutathione of the blood and content of globulins in the serum on the average appear to be higher in euroso-

Table 2

Differences between the Eurosomal and Leptosomal Animals within a Breed

Factors		Three year old colts		Two year old mares		Three year old mares	
		+	−	+	−	+	−
Relative volume of blood cells	*n*	13	12	23	23	10	10
	M	62.7	64.4	55.6	54.4	55.5	62.3
	lim	47.5—77.5	50—77.5	42.5—71	45—70	49—61.2	51—72.5
Dry substance	*n*	14	11	23	22	10	10
	M	23.3	23.6	21.1	21.3	22.1	22.6
	lim	21.4—25.7	20.1—25.5	17.4—24.2	18.3—24.4	20.3—23.3	20.8—23.6
Total glutathione	*n*	14	13	23	22	10	9
	M	70.5	64.4	63.7	63.5	68.03	63.88
	lim	56.13—84.33	30.98—86.81	42.02—75.76	34.36—78.46	54.26—78.99	42.02—73.53
Reduced glutathione	*n*	14	13	23	22	10	9
	M	50.0	47.6	54.4	52.5	53.49	45.19
	lim	40.18—65.03	29.14—61.35	36.19—68.40	26.07—67.30	43.87—63.80	30.37—60.98
Globulins	*n*	5	5	17	15	7	3
	M	3.12	2.88	2.19	1.97	2.78	2.57
	lim	2.67—3.42	2.53—3.00	1.20—3.54	0.68—3.33	1.49—3.67	2.41—2.80

Table 3

Factors	Line of Brimston		Line of Tagor		Line of Hetman
	$n = 10$ ♂♂	$n = 9$ ♀♀	$n = 12$ ♂♂	$n = 13$ ♀♀	$n = 5$ ♂♂
Breathing	11.7	12.2	12.5	13.1	16.4
Pulse	41	41	40	42.5	48.6
Relative volume of blood cells	54.4	55.7	55.8	60.2	61.3
Dry substance	21.5	20.2	22	21.04	—
Catalase activity of the blood	6.25	6.36	6.87	5.96	8.16
Index of the catalase of blood	11.6	11.4	12.2	10.1	13.42
Concentration of the total glutathione of the blood	62.26	58.62	60.55	61.65	66.56
Per cent of the oxidized glutathione	16.8	14.1	17.7	18.1	20.88
Index of the total glutathione	115.2	106.3	108.8	108.4	109.6
Serum proteins	6.64	6.05	6.49	6.52	6.71
Serum viscosity	1.28	1.21	1.33	1.26	1.39
Index Caesari (R.S.E.)	0.50	0.47	0.44	0.35	0.31

mal horses as compared to leptosomal ones. Concentration of the red blood (relative volume of the blood cells and dry substances), content of the oxidized glutathione of the blood and albumins of the serum are on the average higher in leptosomal horses. 3) Physiological differences within a breed were noted in lines of horses of different origin.

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GENETICS

SPEED AND BLOOD VALUE OF ENGLISH RACE-HORSES

By V. I. PATRUSHEV

(Communicated by N. I. Vavilov, Member of the Academy, 8. IV. 1939)

Hippodrome tests of race-horses are among the chief measures for developing speed in particular animals and for evaluating their breed. The possibility of predicting results of tests and training on the basis of a study of the horse has long since engaged the attention of scientific and practical workers, but so far it remains a problem of the future. In order to give a more or less correct prognosis it is necessary at first to study which of the systems of the organism have as their effect the speed of the horse. Our investigations at the Moscow hippodrome in 1938 were directed towards this aim. The blood composition was studied with respect to its carrying function insuring increased metabolism during work. In Table 1 comparative figures are given of the results of the investigation of horses with the highest and lowest speed.

Table 1

Factors	Mares, 2 year old		Colts, 2 year old		Colts, 3 year old	
	+ variants $n = 9$	— variants $n = 10$	+ variants $n = 18$	— variants $n = 12$	+ variants $n = 13$	— variants $n = 11$
Breathing	10.5	13.6	—	—	10	12.5
Pulse	39.4	41.7	42.9	47.4	—	—
Relative volume of blood cells	44.7	42.2	43.7	42.4	54.3	44.6
Sedimentation of erythrocytes (Caesari index)	0.388	0.468	0.419	0.436	0.20	0.30
Total glutathione	64.6	60.6	66.1	62.42	71.10	64.10
Oxidized glutathione	12.92	10.15	13.22	10.73	20.0	13.47
Sugar of the blood	63.1	46.7	56.8	47.4	—	—

The investigations have shown that the fastest horses have a high concentration of the red corpuscles, of the total and oxidized glutathione and also of the sugar in the blood; on the other hand, these horses show a lower index of breathing, pulse and sedimentation of erythrocytes.

Equally representative is the connexion between a number of internal factors and speed when we compare racing results in the plus and minus variant groups (Table 2). The winners in the races have shown on the average a comparatively increased volume of the blood cells, dry substance and total glutathione. It is significant that the blood value of the winners among the

two year group in short distance races does not differ from that of the vanquished. The blood value of the plus and minus variants in regard to speed does not differ in three year old mares except in races for distances of from 2400 m and upwards, in which case the relative volume of the blood cells in the plus variants equals 63.3% and of the minus variants 53.1%, the sedimentation index being 0.31 and 0.51 respectively. The four year old group of colts presents a similar picture.

Table 2

Blood factors	Distances			
	1500 m		1600 m	
	+ $n = 19$	— $n = 20$	+ $n = 11$	— $n = 12$
Relative volume of blood cells	58.7	55	59	54.2
Dry substance	21.9	20.8	21.7	20.8
Globulin content of serum	2.14	1.93	2.28	2.09
Total glutathione	67.1	61.9	66.6	61.6
Sedimentation of erythrocytes (Caesari index per hour)	0.38	0.48	0.39	0.53

We have attempted to detect the physiological differences between stayers and fliers in the group of the fastest horses. We have not been able, however, to trace any difference in regard to most of the factors. True, it has been observed in the case of stayers that compared with fliers they develop a slight tendency to increase the content of total and particularly of oxidized glutathione (Table 3). This we consider as an indication that the tissue of the organism of the stayers as compared with those of the fliers possess a higher oxidizing capacity, and this explains why stayers are able to accomplish a long race without reducing speed. Along with this stayers probably have a number of other, so far unascertained advantages.

Table 3

Name of horses	Total glutathione	Oxidized glutathione
Four year old stayers:		
Angar	83.42	16.55
Sector II	86.49	25.75
Segment	81.28	7.05
Average for stayers:	83.73	16.45
Flier:		
Stog	78.52	2.45
Three year old stayers		
Buynaksk	65.33	5.83
Komar	76.38	19.64
Marsh	65.33	25.76
Espadron	86.81	34.05
Average for stayers:	73.46	21.32
Fliers:		
Bochar	74.23	11.35
Gold Dark	65.03	17.8
Dagar	56.13	15.95
Subbotnik	79.14	16.26
Palvantash	64.72	11.07
Lokaisk	80.06	16.87
Average for fliers:	69.9	14.88

Our opinion as to the physiological systems of the organism will lack accuracy if we limit ourselves to the study of these systems in a state of rest and do not trace their functional changes during strain when the organism is at work. The study of such functional changes should provide an answer to the following two questions:

1) What are the maximum possibilities of increasing function while the organism is under maximum strain?

2) To what an extent are the functional changes in different animals doing the same work productive of economy?

For the purpose of studying functional changes we have examined the horsesbefore the race, immediately after the race and also after a 45 min. rest. Breathing after race was very quick having increased nearly 500%; the pulse nearly 280%. After 45 min. of rest neither the breathing nor the pulse returned to the normal. The relative volume of blood cells increased to 170%, the dry blood substance to 130%.

After work the dry residue of the blood plasma increases from 7—7.5% to 8.2—8.9% and the total number of the serum protein from 6.7 to 8.7%. In the course of 45 min. of rest both these factors return to the normal.

The proportion of albumen and globulin in the serum protein changes under the effect of work. Towards the end of the work the albumen concentration increases, gradually returning to the normal during rest. The globulins in the blood serum decrease after the race. The sugar in the blood is in some cases (two year old horses) reduced after work, but is mostly increased, sometimes twofold, without returning to the normal even after 45 min. of rest.

The catalase activity of the blood increases after the race from 5.1 to 8.5 (in two year old mares); the catalase index is, on the contrary, reduced during work, this pointing to a lesser concentration of the ferment in the reserve erythrocytes. After 45 min. of rest following the races neither of these two factors returns to the normal.

After work the concentration of the total and reduced glutathione shows a sharp increase while in most cases it falls below the normal after 45 min. of rest (Fig. 1). The glutathione content per each erythrocyte is sharply reduced under the effect of work and does not return to the normal during rest.

The curves showing the changes in the concentration of the reduced and oxidized glutathione under the effect of work and rest are indicative of a strongly growing oxygen deficiency during the races (Fig. 2).

The indices of erythrocytes' sedimentation show a sharp decrease after work testifying to an accumulation of hydrolysis products of organic matter in the blood. After the races the concentration of lactic acid increases up to twenty five fold.

The two year old colts Archill and Non-Hetman followed each other closely at the races, Archill beating Non-Hetman by $^7/_8$ of a second. Archill has shown more physiological changes in the main factors than Non-Hetman. In a 1500 m race the two year old mare Argentina beat Ispania by two seconds and showed fewer functional changes which from our point of view testifies to the considerable advantages of this mare.

Palvantash, Soglasny and Chayur, all of them three year old colts, took part in a 2200 m race. In this case the biggest changes were observed also in the horses which developed less speed. The three horses—Gibraltar, Gold Dark and Lokaisk—ran in a 2400 m race. The fastest of them showed the least changes.

Thus, as a rule the best horses show the least changes in the main physiological factors. In other words, the best horses perform their task with greater economy. This, in our opinion, points to the fact that the winners have

other additional advantages and therefore are less in need of a maximum mobilization of the circulating system. From the general point of view these assumed advantages are in the first place to be referred to the cardo-vascular system and the respiratory system.

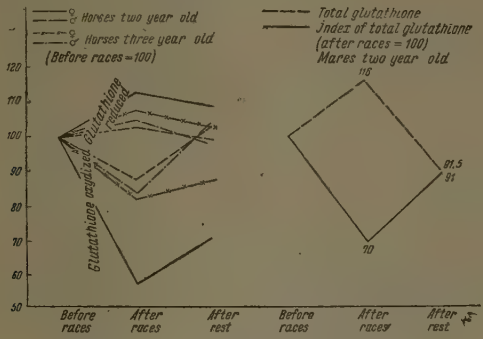

Fig. 1.

Fig. 2.

% of reduced and oxidized glutathione.

On the grounds expounded above one may make the following conclusions:

1. The fastest horses have an increased concentration of the red corpuscles, of the total and oxidized glutathione and of the sugar in the blood. Breathing, pulse and rate of erythrocyte sedimentation prove to be the lowest.

2. The increased concentration of the total and particularly of the oxidized glutathione in stayers points to the best oxidizing capacity of their tissues.

3. In most cases the fastest horses after a race show the least functional changes in blood value.

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GENETICS

PHYSIOLOGICAL VARIATION IN HORSE AS CONNECTED WITH AGE, BREED AND PERFORMANCE

By V. I. PATRUSHEV

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The possibility of tracing the relations between internal factors and performance in farm-livestock is considered to be a most promising outlook in zootechnics. Work in this field reveals the physiological nature of hereditary variation in performance and is, therefore, of theoretical interest. Physiological and biochemical investigations of breed differences may throw light upon the processes of breed-formation and give us more exact knowledge as to variation and inheritance of performance qualities of animals. Besides this, a knowledge of the physiological and biochemical mechanism of hereditary variation in performance may facilitate a more accurate evaluation, selection and breeding of animals. Such are the problems to which we devoted our work carried out at the Moscow hippodrome in 1938. In all, 150 English race-horses, 16 trotters and 13 draft-horses were investigated.

English race-horses are a breed of unsurpassed speed. They are characterized by their asthenic type of constitution and their high neuro-muscular responsiveness. Full growth is attained at comparatively advanced age (about 5 years).

The Ardennes and Brabançons represent the opposite extreme being eurosomal animals adapted for pacing under a great pulling strain. Both these breeds are characterized by earliness and reach the limit of growth at the age of from one and a half to two years.

Russian and American trotters occupy an intermediate position between the English race-horses and draft-horses. Both of these breed groups approach to English race-horses in structure, but are heavier and lack their speed.

Comparative physiological and biochemical investigation may be valuable for disclosing the profound internal peculiarities connected with variation in earliness, types of constitution and trends of performance. From that point of view we have limited our work in its first stage to the study of the haematological complex and to certain indices of cardo-vascular and respiratory system (breathing and pulse). The results obtained are summarized in the table.

The lowest rate of respiration and pulse was recorded for two year old race-horses; draft-horses showed the highest figures, while trotters assumed medium position. Respiration and pulse rate decrease with age: in the case of race-horses it begins to drop at the age of three years, and in the case of trotters at the age of two years. Race-horses possess a relatively large volume of blood

cells and of dry blood residue. Trotters in that respect occupy the second place, draft-horses the third one. The increase of blood concentration with age is more intensive in race-horses than in trotters. Some idea of the differences in the process of blood-formation is provided by the lesser resistance of the young red corpuscles to low concentrations of saline solutions. Investigations have shown that the red corpuscles of two year old draft-horses are less resistant than those of race-horses and trotters. With increase of age the resistance of red corpuscles also increases, this being more manifest in the case of race-horses than of the trotters.

The reaction of sedimentation of erythrocytes furnishes a general characteristic of the blood, reflecting its concentration and composition of plasma. The rate of sedimentation of erythrocytes is higher in draft-horses than in race-horses. With age the difference increase. The velocity of the reaction of sedimentation of erythrocytes is inversely proportional to their concentration, the relation being, however, no absolute one, since the course of reaction is determined by a number of other factors (plasma viscosity, fatigue, etc.). In order to eliminate the influence of different blood concentrations upon the speed of the R. S. E. we compared the R. S. E. indices (ratio of the amount of plasma separating per hour to that separated during 24 hours). The results of analysis have shown that even if due allowance be made for blood concentration, the highest R. S. E. indices are obtained in the case of draft-horses.

Biochemical study of blood concentration has given the following results. The concentration of lactic acid in different breeds is more or less constant in the state of rest. As regards glucose concentration of blood some breed variation was observed for two year old horses. The lowest concentration of blood glucose was found for English race-horses and the highest for draft-horses.

Considerable breed and age variations were recorded for the glutathione content of blood. The concentration of total glutathione in a race-horse blood is about twice as high as that of a draft-horse. Trotters occupy an intermediate position. Respective glutathione content per one erythrocyte in two year old horses of different breeds show the same regularity, though the differences are less expressed.

Glutathione indices in three year old trotters prove to be higher than those of race-horses. This fact is to be accounted for by age variability which differs in trotters and race-horses in connexion with different types of growth and development.

The highest activity of catalase is observed in the blood of draft-horses; the lowest in that of trotters. An intermediate position is occupied by English race-horses. Breed differences as regards the ferment content per one erythrocyte are analogous. The age variability of ferment indices differs for trotters and race-horses and corresponds to the variability of glutathione indices.

The content of non-proteinic substance in the serum increases with age. We have observed slight breed variation in regard to the amount of total serum protein which apparently tends to increase with age.

The amount of albumen in blood serum decreases with age. In all cases stallions possess less albumen that mares. Among two year old colts the albumen content is higher in the case of English race-horses than in the case of Ardennes and Brabançons. Trotters occupy an intermediate position. The opposite picture will be observed as regards the amount of globulin in blood serum. Directly connected with the content of different fractions of protein in the serum is its viscosity which has been recorded as highest for draft-horses and as lowest for race-horses.

Indices	Race-horses			Trotters			Draft-horses Brabançons			Draft-horses Ardennes		
	n	*M*	lim	*n*	*M*	lim	*n*	*M*	lim	*n*	*M*	lim
Breathing	50	14.5	8—44	5	17.2	11—26	6	23.2	19—28	4	19.0	14—24
Pulse	50	43 2	36—64	5	43.8	36—48	6	46.7	40—56	4	39.5	36—44
Relative volume of blood cells	42	48.3	32—57	—	—	—	6	41.3	35—48	5	41.1	38—46
Dry substances of blood	50	21.5	18.0—24.5	5	20.3	19.1—22.3	7	18.5	17.1—19.8	6	18.8	17.5—21.1
Resistance of red corpuscles precipitation	48	62.3	54.0—66	6	63.6	60—66	7	65	62—66	5	64	60—66
Resistance to haemolysis	42	43.2	44—48	6	46	44—54	7	48	46—52	5	49	44—58
Sedimentation of erythrocytes per hour	46	25.7	4—54	5	43	32—55	5	49.2	20—67	3	52.3	44—57
Index Caesari (R.S.E.)	48	0.47	0.06—1.09	6	0.91	0.62—1.37	3	1.72	1.48—2.00	—	—	—
Concentration of blood sugar	42	55.0	11—88	6	63.8	49—78	7	71	42—93	6	76	59—87
Total glutathione	49	65.04	45.7—87.11	6	53.40	46.93—57.46	7	37.80	26.99—42.64	6	40.39	35.56—52.76.
Activity of catalase	50	6.66	4.08—11.39	5	5.32	0.51—8.67	7	10.18	7.82—11.39	6	8.47	7.82—9.35
Albumens of blood serum	33	2.62	0.48—5.01	1	2.84	—	7	2.84	2.32—3.27	5	2.94	3.06—4.06
Globulin content in serum protein (%)	32	52.2	17—91	1	52.7	—	7	55.3	60.0—49.5	5	57.2	40.2—63.7
Serum viscosity	39	1.34	1.08—1.66	5	1.50	1.20—1.75	7	1.66	1.49—2.14	6	1.69	1.48—2.07

There exists for each animal breed group its own specific age variability. This may be shown by the following example. Both globulin content and serum viscosity increase with age. It is significant that draft-horses of two years show higher globulin content than race-horses of the same age. The reason for this phenomenon, it seems to us, lies in the different types of growth and the different constitutions of the horses studied. Such indices as the content of albumens and globulin and the blood serum viscosity which is to a considerable degree determined by them, are related to the general development of the organism and reflect the process of transition of colloids into a state of a coarse dispersion with age. Therefore in early maturing draft-horses the albumen content proves to be the smallest, while the globulin content and serum viscosity are the highest if we compare two year old Brabançons having obtained full growth with race-horses which still continue to grow vigourously.

Differences in breathing and pulse, concentration of red blood, glutathione content etc., are referred by us to hereditary constitutional variation of types of metabolism and spirits of the animals. The high indices of red blood concentration, haemolytical processes and glutathione in race-horses point to a respiratory type of metabolism, highly adapted to the conditions of speedy racing.

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PLANT PHYSIOLOGY

GROWTH OF WOODY PLANTS AS AFFECTED BY CURTAILED DAY LENGTH

By F. L. SHCHEPOTIEV

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Different data have been reported concerning the influence of short days upon growth of woody species. Certain investigators ([2], [6], [7], [8]) conclude that the plants make less growth under short photoperiods. Certain others ([3], [4], [5], [9]) believe them, according to the geographical origin and the nature of the plant concerned, to respond differently and sometimes by increasing growth to the action of short days. The opinion of the first group of students is most widely spread and even in the text-books for high school the short day is treated as an unmistakable factor depressing growth ([1]).

We, however, on the basis of the experimental results here reported must unrestrictedly subscribe to the view advanced by the second group. From our own experiments and the data reported by the above authors ([3], [4], [5], [9]) we deem it very important to apprehend the influence of short days in the proper light, since, as it will be shown farther, we may possibly find here a valuable means to induce growth acceleration in woody species.

In 1935, with the purpose of studying the short day response of woody plants, we set up experiments with ailantus (*Ailanthus glandulosa* Desf.) and white mulberry (*Morus alba* L.) under conditions of Kharkov.

The fruit of ailantus was planted May 15, 1935, seedlings appeared above ground June 11. Photoperiodic treatment set in June 14 and 19. The seed of white mulberry was planted May 15. The seeds were supplied by Krivoy Rog and Bozhedar nurseries, Dnepropetrovsk province of the Ukrainian SSR. Single seedlings appeared June 13—14. Germination was drawn out in time because the beds were uncovered and on that account we began curtailing the day July 4.

It was only within the year 1935 that the seedlings of ailantus and white mulberry were being given short photoperiods (of 6 and 9 hours). Photoperiodic treament lasted 5, 10, 20 days of throughout the vegetation period*.

In a run of four consecutive years the height of the seedlings was measured in all experimental series at the end of vegetation period. Early in September 1938 the leaves were weighed both in ailantus and mulberry. The leaf samples for weighing were taken from all plants in each of the series, without choice but in equal proportion from all parts of a plant top.

* Photoperiodic treatment of short duration is known to have been applied by Lubimenko ([3]) and Eguis ([10]) to herbaceous plants.

From each series there were taken 50 leaves of ailantus and 500 leaves of mulberry. Weighing was done twice at the day of sampling.

The results of 4 year observations are presented in the table. From the table it is evident that it is by increasing stem elongation and leaf weight that the seedlings of ailantus and mulberry respond to very short photoperiods applied during a small length of time. If, however, such photoperiodic action is continued over a long interval, the seedling makes less growth during the first year (Fig. 1) and this depression of growth is noticeable even in 4 year old seedlings. But the same photoperiods (6 hours during 105 days) have induced stronger depression of growth in ailantus than they have done in mulberry which toward the age of 4 years began to get free from the negative influence of short days.

The most important evidence furnished by the data referred to in the table is that a photoperiodic treatment once applied during a short time to the seedlings of ailantus and mulberry extends its growth activating influence over several years.

Therefore the conclusion of Čajlachjan (7), Kramer (2) and others that the effect of short days is only to depress growth in perennials may be ascribed to their having used inadequate methods of investigation. Thus, in the experiments of Čajlachjan and Azbukin (7) the woody seedlings were not tested for their response varying to short days applied during a small length of time, but were subjected to a long treatment (from May till September) with 10-hour days. In Kramer's (2) experiments the action of short photoperiods also lasted a very long time.

Growth of Ailantus and Mulberry in Response to Photoperiodic Treatment Applied Once during that Period of Time

Experimental series	*Ailanthus glandulosa*						*Morus alba*							
	Height of seedlings in cm			Number of seedlings measured in 1938	Weight of 500 leaves in 1938		Seed from	Height of seedlings in cm			Number of seedlings measured in 1938	Weight of 500 leaves in 1938		
	1935	1936	1938		in g	in %		1935	1936	1938		in g	in %
6 h. during 5 days	22.4	74.3	130.8	13	335.1	132.7	Krivoy Rog	—	—	—	—	—	—
6 » » 10 »	33.4	87.2	154.3	17	359.5	142.3		17.3	83.5	174.3	19	182.5	185.0
6 » » 20 »	21.0	78.2	109.6	13	246.7	97.7		9.9	78.9	147.0	17	128.3	130.0
6 » » 105 »	3.6	23.5	37.5	5	47.6	18.8		7.6	82.2	142.1	14	123.4	125.0
Control from Krivoy Rog	24.0	75.6	109.7	19	252.5	110.0		22.8	88.9	164.8	17	98.7	100.0
9 h. during 5 days	40.0	112.0	121.4	24	303.5	120.2	Bozhedar	15.9	51.5	103.5	32	—	—
9 » » 10 »	34.0	83.7	92.6	7	220.3	87.2		13.4	68.7	106.8	18	—	—
Control from Bozhedar	—	—	—	—	—	—		9.2	42.7	86.3	23	—	—

From the first unverified statement that the plants make more growth under longer days Čajlachjan and Zhdanova (8) have come to the second, viz., that there is direct relation between the formation of growth hormone

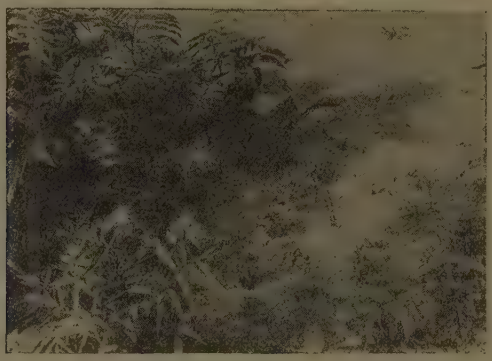

Fig. 1. 'One year old seedlings of ailantus varying in outward appearance according to the duration of treatment with short days. Right—6-hour photoperiod during 105 days; left—6-hour photoperiod during 10 days.

and the length of day. Our experiments, however, as well as those of Shaposhnikov (9) and Moshkov (5) show clearly that this conclusion should not have been made without further inquiry.

Fig. 2. Bed with 4 year old plants of white mulberry. From left to right: 6-hour photoperiod during 1) 20 days, 2) 105 days, 3) 10 days, 4) control, natural day.

Turning to our experiment, we can note a difference between the behaviour of ailantus and mulberry. The increase of growth in the latter is related to the origin of seed and in some of the series has not attained consideralbe value before two years have passed during which it was only slightly noticeable (Fig. 2 represents a bed with 4 year old mulberry seedlings from Krivoy Rog). The stimulating action of short days upon those seedlings has thus shown a delay in rising to a final intensity. Similar results have been attained by

Shaposhnikov (9) in his experiments with *Eucalyptus globulus*. The seedlings of the latter after being treated with 10-hour day length for a period of more than hundred days lagged considerably behind the controls during the first year, but as early as in the second were not only ahead of them in growth but also looked better.

The increase of leaf weight in mulberry has been stimulated by the photoperiodic treatment of short duration with especial strength. It has attained twice its value in control plants. And if we think about the rôle which mulberry leaves play in sericulture, it will be obvious that the possibility of doubling their weight is a factor of supreme economic importance.

What has been reported here may be summarized in the following statements.

1. Curtailed day treatment once applied during a short time to seedlings of some woody species is apt to increase stem elongation and leaf weight by 50 to 100% compared to controls. Not a depression of growth, as certain investigarors believe, but its stimulation is therefore the result of short days applied adequately.

2. If seedlings which had just appeared above ground have been given very short photoperiods (6 to 9 hours) during 5 or 10 days, the stimulation of growth is the result which as in the first year so in the subsequent ones is acting with undiminished strength.

3. The method of short photoperiodic treatment ought to be elaborated for various woody species, since it is easily adaptable for growing woody seedlings in nurseries.

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PLANT PHYSIOLOGY

SOME DATA ON THE CAUSES OF FORMATION OF THE CICATRIZATION LAYER BEFORE THE FALL OF LEAVES

By K. I. GAVRILOV

(Communicated by A. A. Richter, Member of the Academy, 10. IV. 1939)

Experiments and observations have shown that the fall of leaves is closely connected with a number of internal and external factors by whose action it is either accelerated or deferred. Particularly the action of temperature, moisture, light, chemicals etc., have been studied in great detail ([9]).

Anatomical studies have shown that, no matter what causes lead to dropping off of leaves, at the place where the petiole joins stem cicatrization layer is always formed. This layer is set several weeks or days prior to the fall of leaves and represents a plate of newly formed cells distinguished from adjoining lateral cells in having smaller diameter and darker coloration. It becomes further the direct cause of the falling of leaves, since it forms a partition wall across the basal part of the petiole.

It is known that leaves, without falling off, dry out while on the plant, for example owing to spring frosts, summer dry winds, etc. On the other hand, a continued and gradually increasing action of unfavourable meteorological factors, for instance atmospheric or soil drought, may cause formation of the cicatrization layer even in summer, thus leading to the fall of leaves.

For the normal development of the cicatrization layer a certain period of time is necessary; its length depends upon the plant species, on physiological condition, latitude, etc.

At our northern and medium latitudes the fall of leaves usually occurs in October and November. At southern tropical and subtropical latitudes the fall of leaves in certain plant species is often confined to the dryer time of the year. The majority of the evergreen plants drop off leaves continuously, i. e. throughout the year. All these facts demonstrate that the fall of leaves is a complex biological process and that some profound changes occur in the organism of the plant under the influence of a set of internal and external factors; these changes lead to the formation of a cicatrization layer and, as a consequence, to dropping off of leaves. They testify to that fall of leaves is by no means an accident, but is intimately connected with the development of the plant and periodicity of the development.

Aside from dropping leaves, falling of fruits, ovaries, flower buds, etc., are also observed in nature. One may deduce from the available literary evidence that falling of these organs is essentially governed by the same laws ([9,11,3,4]). The question on the dropping off of leaves, fruits, ovaries and flower buds is of considerable interest, both theoretically and practically. The

majority of investigations on the fall of leaves and of reproductive organs was limited up to the present time mainly to collecting facts, mostly of morpho-physiological kind, observed in plants under the influence of climatic conditions; only a small fraction of them takes up the question more seriously, i. e. from the viewpoint of direct study of the region of the cicatrization layer and of the changes which occur there.

Pfeiffer ([11]), applying qualitative reactions for starch and glucose, discovered a strong accumulation of these substances at the base of the peduncle in *Staphylaea* sp. In his opinion, stoppage of assimilates should cause formation of the cicatrization layer. The possibility is not excluded that hormones of cell division of the kind discovered by Haberlandt ([13]) appear at this place. Extensive studies of the recent time have shown that cell division depends on definite substances of the type of hormones which are present in plants in very small quantities. The participation of hormones in the formation of cicatrization layer is not excluded in the sense that they may arise or be transported. An approach from this point of view we find in the studies by Laibach ([7]), La Rue ([6]) and Lockes ([8]).

In our opinion one should have studied another group of phytohormones, the so-called growth hormones of the B-group which are notably hormones of cell division. Our preceding studies have shown this group of substances to play an important part in the development of plants and to be highly variable under the influence of external conditions ([2]). The present investigation was conducted in this direction.

M e t h o d. The study has been conducted on ash, *Fraxinus excelsior*, in autumn 1937 and in autumn 1938.

This material is very appropriate, since it possesses a well formed petiole which has a very well expressed thickening at the joint with the stem; this facilitated taking samples for preparing extracts every time from one and the same place.

The technique of the experiment was as follows. Periodically, beginning by September, several tens of petioles were treated. With the aid of a razor or scalpel the basal part (adjoining to the stem) was excized. Aqueous extracts of 1 : 50 concentration were prepared from the vegetable mass. After three minutes boiling the filtered liquid was tested for growth of yeast in Erlenmeier's retorts containing each 25 cm^3 of Hayduk's nutritive medium. Portions of extract amounted to 2 cm^3 each. Yeast developing under the same conditions but without addition of extract served as control. Each experiment was made in three repetitions. The relative amount of the B-hormone was expressed by the ratio of multiplication of yeast cell after 24 hours as compared to that of the control. Growth was determined with the aid of the counting camera Thoma-Zeiss and expressed in per cent to the control [for technical details see ([1], [12], [2])]. Periodic tests of aqueous extracts for yeast development were intended for tracing dynamics of the B-hormone in the region of the cicatrization layer as connected with the increasing changes in climatic factors. It should be noted that conditions of the autumn in 1937 sharply differed from those in 1938. In the second half of Septemler 1937 temperature increased noticeably whereas at the same time of the year 1938 the mean temperatures showed a striking fall, dropping in some days as low as 2.8° or 2.7°. Sharp fall of temperature of the air produced a material effect upon the further course of events. No gradual appearance of the coloration of leaves was observed. Leaves of some of the trees were shrivelled, became black and fell down. The fall of the leaves in *Fraxinus excelsior* took place in 1938 almost a whole month in advance of 1937.

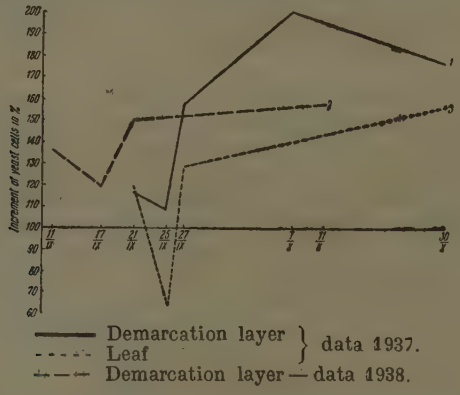
When one compares the gradually increasing changes in climatic factors with the changes taking place in the organism of the plant and, particular-

ly, in the region of the cicatrization layer, one may note that the relative amount of B-substances does not remain unchanged as the fall of leaves approaches (Table 1).

Table 1

Kind of experiment (autumn 1937)	21.IX		25.IX		27.IX		7.X		30.X	
	Quantity of yeast cells	Increment in % to control	Quantity of yeast cells	Increment in % to control	Quantity of yeast cells	Increment in % to control	Quantity of yeast cells	Increment in % to control	Quantity of yeast cells	Increment in % to control
Control	37.0	100.0	37.8	100.0	27.0	100.0	62.5	100.0	86.5	100.0
Addition of the extract from the region of the cicatrization layer	43.4	117.3	41.2	109.0	42.4	157.0	125.0	200.0	151.1	174.6
Addition of the extract from the leaf	44.4	120.0	24.0	63.4	34.8	128.8	—	—	134.0	154.9

Table 1 shows that at the beginning of the process the action of the extracts both from the cicatrization layer and from the leaf exhibits a decrease (figure), the extract from the leaf exerting even a negative effect on the



development of the yeast as compared to control (taken for 100). A similar phenomenon was observed by Oparin and Kuplenskaja ([10]) working on the juice of the sugar beet.

Decrease of the growth substances of the B-group toward the fall of leaves followed by an increase during the fall of leaves could be observed by us not only in leaves and bases of the petiole in *Fraxinus excelsior*, but in leaves of other plant species as well, for example in *Tilia cordata*, *Betula pubescens*, *Ulmus effusa* and *Syringa vulgaris*. This phenomenon is probably connected with an impediment and final ceasing of centripetal flow of sap; however, for the time being we are still in difficulty how to explain such a low minimum which is regularly observed.

As the fall of leaves approaches, the relative amount of the B-hormone rapidly increases. The greatest rise of the curve corresponds to the first third

of October. At this time the beginning of the mass fall of leaves was observed in the plant investigated; on October 8 it dropped off leaves altogether.

The data of 1938 present the same aspect, however, less instructively (Table 2).

Table 2

Kind of experiment (autumn 1938)	11.IX		17.IX		21.IX		11.X	
	Quantity of yeast cells	Increment in % to control	Quantity of yeast cells	Increment in % to control	Quantity of yeast cells	Increment in % to control	Quantity of yeast cells	Increment in % to control
Control	22.0	100.0	15.0	100.0	10.0	100.0	20.0	100.0
Addition of the extract from the region of the cicatrization layer . .	30.0	136.3	19.0	126.6	15.0	150.0	31.5	157.5

This was evidently connected with peculiar features of the autumn of 1938. All the processes were accelerated by the fall of temperature in the latter half of September. *Fraxinus excelsior* dropped off leaves in 1938 nearly one month in advance of 1937, viz., in the period from 21 to 25 September as shown by the corresponding rise of the curve.

On the basis of the data secured we arrive at the following conclusions: 1) Fall of the leaves is a complex biological process. Under the influence of increasing changes in a whole set of internal and external factors profound changes occur in the organism of the plant; these changes lead to the formation of the cicatrization layer and, as a consequence, to the fall of leaves. 2) Formation of the cicatrization layer is mutually connected with accumulation of B-hormones in its vicinity. 3) As the fall of leaves approaches, the relative amount of the B-hormone rapidly increases in the region of the cicatrization layer; it reaches its maximum and is maintained at a rather high level during all the period of the fall of leaves.

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ZOOLOGY

NEW DATA ON THE ECOLOGY AND DISTRIBUTION OF FISH IN THE LAPTEV SEA

By A. P. ANDRIASHEV

(Communicated by S. A. Zernov, Member of the Academy, 25. III. 1939)

During the recent years in connexion with gaining masters over the Northern-Sea Route, the exploration of the Soviet Sector of the Arctic was considerably intensified which was extended to one of the least studied of our arctic seas—the Laptev Sea. Among others, a hydrographical expedition on the ice-breaker «Malygin» was working in the Laptev Sea during the summer 1937. During the cruise the author took 40 benthonic stations, mainly in the southern part of the sea, as well as in the Vilkizki strait and in the western part of the East-Siberian Sea. In all 315 specimens of fish were caught (on 23 stations) belonging to 15 marine species. Among them were several species new to these little explored seas: *Myoxocephalus verrucosus*, *Lycodes jugoricus*, *Lumpenus medius* and the species *Triglops pingelii*, *Ulcina olriki* and others recently discovered by V. K. Essipov (in litt.).

Icelus spatula spatula Gilb. et Burke. Our specimens of this arcto-boreal, far-eastern species were caught northwards from the Lena delta, at a depth of 25—28 m, on a muddy sand ground, at a bottom temperature from—0.7 to —0.8° and a bottom salinity of 25.3—25.7‰. One specimen was caught in the western part of the Eeast-Siberian Sea, hitherto no finds of this species were reported from that sea.

Triglops pingelii (Reinch.) subsp. *Triglops pingelii* with a pacific form *beani* was considered formerly as a species with an interrupted distribution. The occurrence of *Triglops pingelii* in the Laptev Sea renders doubtful its being an amphiboreal species, and makes us consider it a widespread arcto-boreal species. Our 13 young specimens (length up to 104 mm) were caught northwards of the Lena delta, at a depth of 13—14 m, on a muddy sand ground, at—0.9°, and a salinity of 23.1‰. According to a series of characters, they belong rather to the eastern form (*Tr. pingelii beani* Gilb.) than to the Barentz Sea form.

Myoxocephalus verrucosus (Bean) was recorded formerly only in the Chukotsk, Barentz and Okhotsk seas. We discovered it for the first time in the brackwater zone of the Lena delta, at a depth of 9.5—14 m, on a muddy sand ground, at a temperature from—0.6 to—0.9° and a salinity of 15.0—23.0‰. Our specimens are not to be distinguished from the far-eastern form. Information about a find of *M. scorpius* off the Novosiberian islands is due to an error. The specimens from Kotelny island (Inst. of Zoology, №14210 and 14211, the Nerpichia bay 1902) examined by us belong to the far-eastern species *M. verrucosus*. This arcto-boreal species (more exactly arcto-northern-boreal) is indubitably a pacific immigrant who, like both preceding species, penetrated into the northern seas during the post-glacial period.

Myoxocephalus quadricornis labradoricus (Gir.). This circumpolar high-arctic species was encountered northwards of the Lena delta under conditions similar to those of the preceding species. They feed on *Mesidothea sibirica* and, nearer to the shore, on *M. entomon glacialis*.

Artediellus scaber Knip. was found in the Kara, Laptev and East-Siberian Seas. Of interest is the occurrence of this high-arctic marine species in the greatly diluted and warm waters near Dixon island at a depth of 8—10 m where the influence of the Yenissey water is very noticeable, at a temperature of 4.7—5.3° and a salinity of 7.1—15.5‰. The specimens from the Laptev and the East-Siberian Seas are nearer to the Chukotsk and Anadyr (North Bering Sea) forms than those of the Kara Sea, forming a full transition from western to eastern forms.

Gymnocanthus tricuspis (Reinh.). Our collections comprise about 120 specimens of this circumpolar pan-arctic species from the southern part of the Laptev Sea at a depth of 9—28 m, on a muddy or muddy-sand bottom, at a $t°$ from—0.6 to—1.2° and a salinity of 16.1—25.7‰. Length from 20 to 150 mm.

Ulcina olriki (Lütk.). A high-arctic circumpolar species*. Our specimens were obtained in the south-western part of the Laptev Sea, northwards of the Lena delta, at a depth of 23—28 m, at a temperature from—0.7 to—1.3° and a salinity of 25.3—27.3‰. Length up to 69 mm.

Liparis koefoedi Parr. Specimens belonging to this species were caught off Russky island at a depth of 72—75 m, on a muddy ground with ferro-manganese concretions, at a temperature of—1.8° and a salinity of 34.3‰. Besides these specimens we found in the Laptev and East-Siberian Seas the young specimens of *Liparis* (27—33 mm) with a lesser number of fin-rays and a small eye, as in *Liparis liparis*.

Lumpenus medius (Reinh.). Hitherto was not recorded in the Laptev Sea. Our specimens were taken northwards of the estuarine zone of Lena delta at a depth of 28—32m, at a temperature from—0.8 to—1.4° and a salinity of 25.3—29. 1‰. This species should be considered as an arcto-boreal species of pacific origin, rather than an arctic one.

Lycodes polaris (Sabine). A high-arctic circumpolar species, usually known as *L. agnostus* Jens. (also *L. turneri* Bean.). We found it in the Laptev and East-Siberian Seas at a depth of 22—29 m, on a muddy and muddy-sand bottom, at a temperature from—0.7 to—1.4° and a salinity of 25.3—27.7‰. Shorewards in the estuarine zone of our Siberian seas it is replaced by the following species.

Lycodes jugoricus Knip. Until now this species was known only by two young specimens (from the strait Jugorsky Shar and the adjacent part of the Barentz Sea). Recorded in the White Sea too. Our collection contains two** specimens (one of them adult) of this species, which proved to be very characteristic. Both were caught near the Lena delta at a depth of 12.5—14 m, at a temperature from—0.8 to—0.9° and a salinity of 15.0—23‰. The characters of this species are as follows: *D* 99, *A* 78, *P* 17, *Vert.* 99. They have peculiar chin crests which in front grow together, but not completely, since the tips of both crests stand out like two small tubercles (in young fishes the crests are only very near to one another). The mucous pits are very deep and separated one from another. The teeth on the vomer are blunt and very numerous, they form a platform composed by 11—14 teeth. The body is nacked. The lateral line is mediolateral. The pectoral fins are large, 16.5% *L*, the ventral 4.1% *L*, 18.7% of the head. The colour is very typical—ground colour light (yellowish) with 8—9 narrow blackish-brown bands broadening upwards; these bands are narrower than the clear interspaces.

Lycodes pallidus Collett. Our specimen from Russky island does not differ from the usual forms. A less known species, *L. attenuatus* Knip. is

* As yet not reported either from the East-Siberian Sea or the American sector of the Arctic.

** One specimen of this species from Kotelny island is in the collection of the Zoological Institute of the Acad. of Sciences (*L. agnostus*, identified by N. M. Knipowitsch).

recorded in the Laptev Sea; this can at most be considered as a local form of the widely distributed *L. pallidus*. We will not dwell on other better known species of our collection.

Plotting on a map the leading benthonic forms, a very pronounced change in the fauna is observed in the region of the Lena delta, which coincides well with changes in depths and salinities. The boundary lies on the edge of a 15 m terrace (isobath 15—20 m) with a bottom salinity of 23—24‰. Northwards of this boundary* is spread a marine fauna (bearing traces of a lowered salinity) comprising many species usual for the northern seas, including *Decapoda* and *Echinodermata*. The most frequent are: *Eualus gaimardii beltcheri*, *Sabinea septencarinata*, *Stegophiura nodosa*, *Ophiura sarsi*, *Cucumaria glacialis*, *Yoldia hyperborea*, *Nucula tenuis*, *Munnopsis typica*, *Arrhis phyllonyx*, *Synidothea bicuspida*, and many others. Shorewards, at a depth of 9—14 m, bottom salinity of 15—23‰ and a somewhat higher temperature is encountered a fauna of a more estuarine type with a complete absence of *Decapoda* and *Echinodermata*, but with huge quantities of *Nephthys longosetosa*, *Mysis oculata*, *Ampelisca macrocephala*, *Acanthosrepheia behringensis*, *Monoculodes borealis*, *Onisimus derjugini*, *O. affinis*, *Mesidothea entomon glacialis*** and others (benth. st. No. 28—36 and 38). To the ichtyofauna of the marine type belong: *Lycodes polaris*, *Gymnelis viridis*, *Icelus spatula spatula*, *Ulcina olriki*, *Lumpenus medius* and others. The estuarine zone of the shoaleness is characterized by *Myoxocephalus quadricornis labradoricus*, *M. verrucosus*, *Lycodes jugoricus*, *Liopsetta glacialis*, *Arctogadus borissovi* and, partly, *Gymnocanthus tricuspis* and *Artediellus scaber*, which are usually also met under more marine conditions.

According to recent data the ichtyofauna of the Laptev Sea consists of 31 species*** (31 species with the possible *Careproctus reinhardii*). Twenty of them belong to the group of marine and mainly marine species, while the remaining eleven are to a considerable degree connected with fresh waters. Faunistically the basic group is composed by species of the arcto-circumpolar region, among them: the endemics of the Siberian seas, the circumpolar species and even more widespread species apparently connected by their origin with the Far-east rather than with Arctic seas. The second group is composed by some migrants of the North Pacific fauna, who penetrated into the Laptev Sea during the post-glacial period. The third group comprises the species characteristic for the North Atlantic sector of the Arctic, who penetrated into the Laptev Sea from the West. And finally, the fourth and least known group is formed by the deep water forms of the Polar basin. From the stand point of zoogeographical divisions, the ichtyofauna of the Laptev Sea should be characterized as a highly arctic one. Boreal types are totally absent, the mainly boreal occur in small numbers (6.3%), the widespread arcto-boreal species are more numerous (31.2%); however, the bulk is formed by arctic species (62.5%). Thus, the main stock of the ichtyofauna of the Laptev Sea consists of arctic species of the North Polar Sea fauna, with an admixture of Atlantic and Pacific elements, the both latter being far less numerous in the Laptev Sea than in other northern seas of the Soviet Union.

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* It should be noted that the ecological boundary established by us is in rather far agreement with the purely physical boundary of brackish and marine waters (24.7%).

** According to E. F. Gurjanova's determination, *Amphipoda* and *Isopoda*.

*** Besides the species of the deep water fauna of the Polar basin, these can be found in the deep trough eastwards of the Severnaja Zemlya, and in general in the northern part of the Laptev Sea.

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DEVELOPMENT MECHANICS

STUDIES BY THE METHOD OF TRANSPLANTATION ON THE LOSS AND RESTORATION OF THE REGENERATIVE POWER IN THE TAILLESS AMPHIBIAN LIMBS

By L. W. POLEŽAJEW and G. I. GINZBURG

(Communicated by I. I. Schmalhausen, Member of the Academy, 26. III. 1939)

Guyénot ([5]) and Liosner ([7]) have shown, the former xenoplastically, the latter homoplastically, that the limbs'regenerative power persists after they have been transplanted to animals having lost this ability, whereas the limbs having lost the regenerative power cannot regenerate even after being transplanted to animals which have the power of regeneration. Using another method, Poležajew ([8], [9], [10], [11]) similarly came to the conclusion that the limbs are able to regenerate, if acted upon by the humoral medium of animals which have lost regenerative power. Later on, Borssuk ([2],[3]) was led to conclude that the humoral medium of tadpoles, with the regenerative power lost, inhibits the process of limbs, regeneration. This conclusion, however, cannot be regarded as significant, owing to paucity of material and the imperfectness of technique (stages were used which little differed as to their regenerative power).

Liosner ([7]) put forward the question as to the possibility of an inhibitory or stimulating effect of the limb transplantation on its regenerative power. He has shown the latter alternative to be true: in 4 cases out of 37 the leg autotransplanted has regenerated, while the pair leg operated at the same time and left in its place did not regenerate.

Poležajew ([8],[9],[10],[11]) advanced the question as to the restoration of the regenerative power. By applying the method of traumatization he succeeded to restore the accumulation phase of the regenerative material and to obtain the regeneration of the experimental leg, while the control leg which had not been submitted to traumatization failed to do so.

Jakovleva ([12]), having reproduced the above-mentioned experiment of Liosner, came to the conclusion that «transplantation is not a factor which can make a limb regenerate at a stage when this power is already lost». This inference is founded on a misunderstanding apparently due to defective technique of the operations or to lack of precision in the determination of stages, which has already been pointed out by us ([14]). We also have reproduced Liosner's experiments, and the results proved in 50% of cases to be positive.

In the present work have been advanced and experimentally investigated the following questions:

1. Are the phenomena brought about by means of transplantation and traumatization of the limbs and leading to the restoration of their regenerative power similar or different?

Operation	Operated	Fixed at early stages	Remained	1 No leg has regenerated	2 Both legs have regenerated	3 Both legs have partly regenerated	4 The experimental leg has regenerated, the control one has not	5 The control leg has regenerated, the experimental one has not
Autotransplantations at stage I	150	3	80	—	70	1	—	2
Autotransplantations into the back at stage IIa	39	3	30	1	9	—	11	—
Autotransplantations into the tail at stage IIa	34	4	26	5	8	1	4	1
Total: autotransplantations at stage IIa	73	7	56	6	17	1	15	1
Transplantations into the back from the stage IIa to stage IIIa	102	19	65	24	7	—	3	20
Transplantations into the tail from stage IIa to stage IIIa	113	27	61	27	5	—	2	18
Total: transplantations from stage IIa to stage IIIa	215	46	126	51	12	—	5	38

2. What is the way in which the graft affects the regenerative power, and is its influence the same at various stages of the transplanted organ's development?

3. Does the humoral medium alter the limb's regenerative power in the course of the metamorphosis of tailless amphibians?

4. Does the recipient's region of transplantation («regionality») affect the limb's regenerative power?

The experiment has been carried out on tadpoles of *Rana temporaria* in the summer 1938. The following stages have been chosen: I—thigh and shank are not yet articulated at the knee-joint; IIa—thigh and shank meet at an obtuse angle, rudiments of the digits are clearly pronounced; limbs are developed to a slight degree (at the stage IIb the limbs are strongly developed); IIIa—thigh and shank are strongly developed and form an acute angle. In case of simple amputation, the limbs regenerate at the proximal part of the shank at the stage I in 90% of cases, at the stage IIa in 42% of cases, at the stage IIb in 4%, while at the stage IIIa they do not regenerate at all (14).

The experiment was carried out in the following manner. The right hind leg was amputated in the proximal part of the shank and then near the trunk. Skin was taken off the thigh of the stump amputated, and the part of the limb laid bare was transplanted under the skin of the abdomen, of the back or of the tail, within their proximal third. In 100% of cases the graft was quite successful. For control purposes there also was amputated the left hind leg of the donor on the same level, i. e. in the proximal part of the shank.

6	7	8	9	Results of regeneration			
				+		−	
The experimental leg has regenerated completely, the control one partly	The control leg has regenerated completely, the experimental one partly	The experimental leg has regenerated partly, the control one has not at all	The control leg has regenerated partly, the experimental one has not at all	Number of cases	%	Number of cases	%
5	1	1	—	6	7.5	3	3.7
7	1	1	—	19	63.3	1	3.3
—	—	6	1	10	38.5	2	7.7
7	1	7	1	29	51.8	3	5.4
2	2	2	5	7	10.8	27	41.5
1	4	—	4	3	4.9	26	42.6
3	6	2	9	10	7.9	53	42.1

The control was individual, i. e. in cases of homoplastic transplantation each experimental tadpole had its respective control. The results of regeneration were considered as positive (+), when the experimental leg regenerated better than the control one, and as negative (—), when the former regenerated worse than the latter.

In nearly all cases, the transplants were vividly reddened on account of a considerable accumulation of blood in them; this phenomenon was observable within 15 days from the moment of operation. The results of the operation are summarized in the table.

The data given in columns 4,6 and 8 of the table are classed as positive (+), while the data in columns 5,7 and 9 are referred to negative ones (—). The negative results may be accounted for by the fact that in a certain per cent of cases the regeneration of one leg may even in simple amputations proceed with better success than the regeneration of the other, the ratio being the same both for the right and the left leg (14).

The data given in the table show that limb autotransplantation at the first stage does not stimulate regeneration: there are 7.5% of positive results against 3.7% of negative ones; at the stage IIa, limb autotransplantation brings about restoration of the regenerative power: we have 51.8% of positive results against 5.4% of negative ones; limb homotransplantation from stage IIa to stage IIIa brings about inhibition of the regenerative power: 7.9% of positive results stand against 42.1% of negative ones.

Histological examination revealed the following. In a control at stage IIa subjected to simple limb amputation, the tissue differentiation is pre-

served in its essential features: the skeleton does not disintegrate, the muscle patterns maintain their integrity; mesodermal cells of the regeneration rudiment do not accumulate on the amputation wound surface under the epithelium. In case of limb autotransplantation, dedifferentiation of tissues takes place: cartilaginous epiphyses are transformed into dense mesenchymatous thickenings; muscle patterns disintegrate, forming a homogeneous mass of mesenchymatous cells which, assuming a round shape and moving towards the epithelium of the amputation wound surface, form the mesodermal part of the regenerating rudiment. Similar phenomena of tissue dedifferentiation, accompanied by a still greater disintegration of skeleton, and a similar mode of the regenerating rudiment development are observed to accompany the restoration of the limb's regenerative power in tadpoles brought about by the method of traumatization ([10],[11],[15]). Positive results of regeneration through autotransplantation were observed in 51.8% of cases, and those obtained through traumatization—in 49.8% of cases. Thus, we have here an additional example pointing to the fact that various equifinal processes are essentially determined by the same factors [principle of equifinality ([13])].

Transplantation at stage I brings about a delay in the development and regeneration of the limbs, as compared with the control. In transplantation made at this stage Jakovleva ([19]) has also observed a delay in the limb development, and, moreover, dedifferentiation of the skeleton.

In case of limb transplantation from stage IIa to stage IIIa, the limb differentiation mostly persists. However, in a number of cases dedifferentiation is to be observed, which mostly occurs at the cost of muscle patterns; the latter disintegrate into a mass of isolated rounded cells forming no regenerative rudiment. Thus, the tadpoles' humoral medium inhibits, in the course of the metamorphosis, the limb's regenerative power, stimulating, on the one hand, the tissue's differentiation, and on the other, altering the cell's properties.

In a number of cases it was observed that muscle patterns disintegrated in the course of their differentiation, and huge centers of formal blood elements appeared in the place of disintegration. This picture may suggest that these elements had formed at the expense of the altered muscle patterns. It is precisely in this manner that Weizmann ([18]) explains similar phenomena. These data should be carefully studied to enable of more definite conclusions.

The loss of limb regenerative power in tadpoles takes place not at once; first, it is caused by tissue differentiation proceeding while the cell's regenerative power still persists; further on, it is caused by the alteration of cell properties. The method of the regenerative power restoration (through traumatization, transplantation) is at present reduced to changes produced in the histological, and not in the cytological, differentiation.

The data of the table show that the recipient's regionality exerts an influence upon the regenerative power of the organs transplanted: the limbs regenerate less successfully on the tail than on the back. According to data by Blacher, Worontzowa and Liosner ([1]), the limbs transplanted grow on the tail better than on the back. Therefrom we conclude that the organs which are resorbed in the course of metamorphosis (tail), affect regeneration and growth in a different way. This may be easily understood, since regeneration is not confined to the growth of tissues, and at early stages it proceeds essentially without proliferation ([10],[11],[12],[15],[16],[17]).

Six cases were observed, which have not been included into the table, where the limbs transplanted brought forth fin-shaped (tail-like) organs upon the tail. Guyénot et Schotté ([6]) have obtained the formation of such organs by drawing aside the nerve of the limb. In our cases, it was the trans-

plant that played the part of nerve. The cellular material of the lateral surface of the tail shrank under the epithelium upon the amputation wound surface of the limb transplanted, and developed, according to its potencies, into a tail-like organ, in spite of its direct contact with the limb tissues. This fact is perfectly consistent with our previous observations on the development of young regenerative blastems of the axolotl tail transplanted into the limb region ([12],[16],[17]), while it contradicts Efimov's assumption ([4]) that in his experiment, similar to ours, the mesodermal tissues of the tail had contributed to the building of the limb regenerated in tadpoles of *Rana ridibunda*, the ontogenetic limits of which in regard of regenerative power are not f xed.

Conclusions

1. Autotransplantation at the stage IIa brings about dedifferentiation of tissues mostly of muscle patterns, restoration of the phase of accumulation of cellular material in the regenerative rudiment, and a complete regeneration of the limb, the tissues of which do not dedifferentiate.

2. Changes leading to the restoration of limb regenerative power in tadpoles, are essentially the same in the case of transplantations associated with traumatization.

3. Autotransplantations at the stage I bring about a delay of the limb development and regeneration.

4. Homoplastic transplantations from the stage IIa to the stage IIIa bring about inhibition of regenerative power in the limbs under the action of the animal humoral medium, in case of the latter having lost regenerative power.

5. The loss of limb regenerative power in tadpoles depends at first upon the progress of tissues differentiation and afterwards upon changes in the cells. Restoration of regenerative power through method of transplantation and traumatization is possible only in case if stable, non-reversible changes have yet not occurred in the cells.

6. Organs (tail) resorbed in the course of metamorphosis inhibit the limb's regenerative power while, none the less, stimulating the limb growth. Various regions of transplantation (back, tail) affect the regeneration process differently.

7. The transplanted legs may induce the tail tissues to form fin-shaped (tail-like) organs. At the same time, the potencies of the cells in tail tissues do not change in character, regardless of their intimate contact with the tissues of the amputation wound surface of the limb.

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PALEONTOLOGY

DEVONIC FLORA FROM NORTH-EASTERN BALKHASH REGIONS (KAZAKHSTAN)

By M. F. NEIBURG

(Communicated by V. A. Obruchev, Member of the Academy, 1. IV. 1939)

Deposits of the Devonian widely developed in north-eastern Kazakhstan as well as in adjoining regions of Siberia, are usually characterized by abundant marine fauna; while traces of non-marine life represented by plant remains from corresponding facies of the Devonian on the above-mentioned territory have been thus far rather scanty. Thus, we are still unable to approach the question of development of the Devonic flora on this vast territory, both in time and range, and consequently, that of synchronization of corresponding deposits; as a matter of fact, we are not sufficiently familiar with the composition of this flora. Therefore any finds likely to supplement our knowledge in this field are of interest, and care should be taken to record them.

From this viewpoint, a valuable contribution has been made by collections of plant remains, furnished and turned over to me for study by a group of geologists of the Geological Department of the Kazakhstan Branch of the Academy of Sciences of the USSR—V. A. Vakhromeev, V. S. Dmitrievsky, D. F. Loginov, I. P. Novokhatsky and V. M. Sergievsky (1936, 1937, 1938 collections). These collections assume all the more importance, since they have been obtained from sections, wherein layers with plant remains are intercelated with layers containing marine fauna, and sometimes the fauna and flora occur in the same pieces of rocks. The purpose of this communication is to furnish preliminary data on the plant remains, gathered at different points and from separate sections of the north-eastern Balkhash regions.

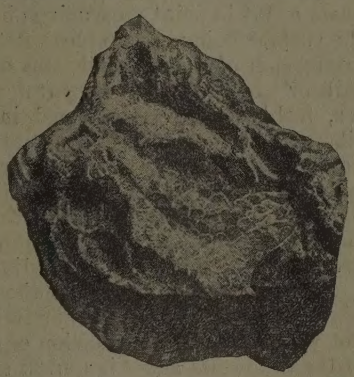
A composite normal section prepared by the geologists of the above-named Branch comprises beds of Paleozoic sediments a few kilometers thick. Abundant plant remains are referred to the upper part of the section, with a thickness of about 6000—6500 m, to the upper horizons of the Shointass and overlying Ainabulak series, composed in the main of cherty rocks (silt and shales), sandstones, graywacke, with intercalations of limestones, tuffs, porphyries; plant remains occur both in cherty rocks and in sandstones. As to the time measures of this section subdivided on faunal evidence, on the basis of various groups of animals (brachiopods, bryozoans, corals)*, such subdivisions do not coincide pointing in general to the period within D_1 to C_1. Plant remains obtained from the above-mentioned series present large numbers of specimens belonging to a relatively small number of species. It should be emphasized on this occasion that the situation within the normal section of a number of places containing the flora is still rather obscure. For this reason it would be too early to attempt a determination of the sequence of forms and of the time measures of this thick accumulation of sediments on the basis of the foregoing material alone, and being guided merely by some or other „leading" type genera, or species restricted to a definite division of the Devonian, according to sections of Western Europe.

* According to V. M. Sergievsky's private information, provisional determinations of fauna have been made by A. A. Bublichenko, V. P. Nekhoroshev and E. D. Soshkina respectively.

Therefore, for the time being, until it will be possible to correlate strictly the locality of the flora with the normal section in which the stratigraphic succession of layers would be beyond any doubt, only the general composition of the flora of the Shointass and Ainabulak series in the north-eastern Balkhash regions, and the general significance of its age may be discussed.

Remains of primitive *Lepidophytes* are most widely distributed throughout the section, those designated as *Leptophloeum australe* McCoy and *L.* cnf. *sibiricum* Krysht. being particularly common.

The Kazakhstan samples of the former are indistinguishable from those described by Feistmantel from Australia, from Upper Devonian strata, or beds passing from the Devonian into the Carboniferous, under the name of *Lepidodendron nothum* Ung., and which are now identified with *Leptophloeum australe* McCoy. Impressions defined as *Leptophloeum* cnf. *sibiricum* Krysht. will probably prove to be identical with *L. sibiricum* Krysht. from the Lower Devonian (Koblenz) of the Minussinsk basin. According to private information of Novokhatsky based on his field observations, *L.* cnf. *sibiricum* had made its appearance along the section somewhat earlier than *L. australe*. It is likewise curious that some of the impressions from Kazakhstan referred to *L.* cnf. *sibiricum* are greatly resembling some of the specimens known under the name of *Angarodendron obrutchevi* Zal. from the base of the first series of the Kuznetzk basin and from the series H_0—H_2 of the Minussinsk basin. The question suggests itself whether any genetic relationship is possible between these coal deposit representatives of *Lepidophytes*, hitherto known but from Soviet Asia, and more primitive representatives of this group from the Devonian. In this connexion it may be appropriate to mention that Prof. Kräusel, the renown authority of Devonic flora of Western Europe, deems the *Leptophloeum* and *Tomistachys thyrsiculus* Zal. described from the same series of the Kuznetzk basin to be not too distant relatives. Among other impressions have been met leaf-cushioned *Lepidodendron*, provisionally designated by the name of *L. acuminatum* Goepp. aff. and cnf. *L. nathorsti* Kidst., as well as *Knorria* and *Stigmaria*, further equivocal impressions, which might be referred to cnf. *Lyginodendron Sverdrupi* Nath., nuclei of *Asterocalamites scrobiculatus* Schloth.



Parka cf. *decipiens* Flemming. North-eastern Balkhash regions, Ush-Tyube. Drawn from a sample of I. P. Novokhatsky's collection ($^1/_1$).

The enumerated forms are in general peculiar to D_3—C_1. In great profusion occur imprints of shoots with leaf bases which may be safely assigned to the genus *Barrandeina* Stur. and even to *B. dusliana* (Kr.) Stur., a species quoted from the Middle Devonian of Bohemia. Sporogenous shoots and the outline of the leaf blade known to be peculiar to this specimen from Bohemia have not been found among the Kazakhstan materials; therefore it is difficult to assert their specific identity. Further, fructiferous shoots should be mentioned to be referred to a new species of the genus *Barinophyton* White, known from the Upper Devonian of Belgium, eastern Canada and Australia. There are impressions of shoots to be classed indubitably with *Hyenia* Nath. which are indeed hardly discernible from *H. sphenophylloides* Nath.; the genus is generally considered as characteristic of the Middle Devonian of Western Europe and North America, however, it is also quoted by Zalessky

in conjunction with the eastern slope of the Urals, from deposits relegated by him to the base of the Upper Devonian. It is a matter for regret that the Kazakhstan materials lack impressions which could be safely placed among *Psilophytales*, characteristic of the Lower Devonian, as the available imprints of fragments of stalks, sometimes with primary bifurcation, other characters lacking, could be referred to *Archaeoptris* pointing to higher horizons.

Finally, special mention should be made of one impression from the collection of Novokhatsky from the mud-volcano Ush-Tyube at the lake Tuzkul, which in my estimation can be safely assigned to the genus *Parka* Fleming, thus far known by one species *P. decipiens* Flem. from the Lower Devonian of Scotland and England alone. A plate of fine-grained sandstone bears a flat imprint measuring about 2.5 × 1.5 cm with an indistinct outline; the surface being covered by a network of cells, it could be assumed to be the impression of a part of thallus of the above-mentioned plant (figure). The cells or discs are oval or pentahedral in outline, from 0.2 to 0.3 cm in diameter, feebly concave, arranged in close contact with each other, with thin ribs extending along the lines of fusion of cells with one another. There are no remains of organic matter present. Maceration of the rock in search of spores has not yielded any positive results, however, by the general aspect by the form and dimensions of the discs which may be considered as impressions of sporangia, the said imprint fully agrees with the description and drawings which refer to the indicated monotype genus.

Thus, taking into account the time equivalent of the described forms according to sections of other countries, and being that in this respect we have not yet established a criterion of our own, applying to our territory, the flora of the Shointass and Ainabulak series of the north-western Balkhash regions is evidently not uniform in age and, most probably, mainly refers both to the Middle and Upper Devonian, ensuing, perhaps, yet from the top of the Lower Devonian (*Leptophloeum sibiricum*, *Parka*), on one hand, and containing into the base of the Carboniferous, on the other (*Leptophloeum australe*, bead-cushioned *Lepidodendron* etc.).

As regards both the specific composition and age, we should expect to shed more light on the question upon further detailed treatment of the material, coupled with a respective correlation of the localities with the normal geological section. If we recall that A. N. Krishtofovich indicates five forms from the Kirghiz steppe, namely: *Duisbergia mirabilis* Kr. et Weyl., *Asteroxylon sibiricum* Krysht., *Arthrostigma* sp., *Aneurophyton germanicum* Kr. et Weyl., *Barrandein kirghizica* Krysht., furnishing ground for his assigning the corresponding deposits to the Middle Devonian, we should believe the composition of the Devonian flora of Kazakhstan to be greatly supplemented by the above-described material. Furthermore, it should be noted that in 1921 V. A. Khakhlov published a list of forms of the Upper Devonian (after Khakhlov) flora from the south-western coast of lake Balkhash; however, too sketchy drawings illustrating this work prevent us from making comparisons, and we would merely suggest that, e. g., the new generic name introduced by the author is probably a synonym of *Leptophloeum australe* McCoy.

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